THESIS FOR THE DEGREE OF LICENTIATE OF ENGINEERING

# Environmental, health and safety assessment of phase-change solvents for post combustion $CO_2$ capture

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# Abstract

A novel class of solvents exhibiting liquid-liquid phase separation upon reaction with $CO_2$ and/or change in temperature, promises significant reduction of energy requirement of the post combustion capture by chemical absorption. However, proceeding to a large-scale application of novel materials requires holistic evaluation of the aspects related to human health, safety, and environmental impacts currently missing for phase-change solvent alternatives. The current work addresses the gap by performing such an evaluation by help of combined life cycle (LCA) and environmental, health and safety hazard (EHS) assessment. The evaluation is done at the substance level, during the process of design and selection of the solvent alternatives by computer-aided molecular design (CAMD), and the process level, estimating the impact of the capture system deploying phase-change solvents.

The integration of the LCA and EHS impact criteria into the solvent design procedure leads to identification of a much wider set of optimal solvent structures compared to having only thermodynamic properties as objective functions in CAMD. The search enriched the Pareto fronts with the -OH group containing structures beneficial in terms of their lower impact. On one hand, such molecules are highly soluble in water, thus they might not be the best option from the phase-change perspective. On the other hand, there are OH-containing amines proven to exhibit liquid-liquid separation, which have so far received considerably less attention and might require further investigation.

The process level assessment showed that phase-change solvent systems have a potential to be a better alternative to the conventional amine solvent systems due to the reduced reboiler duty and possible lower impact on the environment. Less mobile solvents might be preferable with respect to human safety. With respect to long-term impacts, the process design of the capture systems with the phase-change solvents might promote accumulation of carcinogenic nitrosamines, thus their concentration should be monitored. The life cycle impact was mostly defined by the steam requirement for solvent regeneration and electricity demand for cooling media delivery. The use of renewable electricity and industrial waste heat can decrease the LCA impact of the phase-change capture plant by 70-90%. Then, the remaining impact will be dominated by the degradation behaviour of the solvent molecules, which emphasizes the benefit of the solvents displaying low degradation rates and highlights the importance of experimental studies addressing the degradation behaviour of the solvents.

***Keywords:*** carbon capture, phase-change solvents, LCA, EHS, CAMD

# List of publications

This thesis is based on the following papers:

**I.** Shavalieva, G., Papadopoulos, A.I., Badr, S., Seferlis, P., Papadokonstantakis, S., 2018, Sustainability assessment using local lazy learning: The case of post-combustion $CO_2$ capture solvents, *Proceedings of the Process Systems Engineering Conference, PSE 2018, 1-5 July 2018, San Diego, USA* (peer-reviewed), doi: 10.1016/B978-0-444-64241-7.50132-4

**II.** Papadopoulos, A.I., Shavalieva, G., Papadokonstantakis, S., Seferlis, P., 2019, An approach for simultaneous computer-aided molecular design with holistic sustainability assessment: Application to phase-change $CO_2$ capture solvents, *Computers & Chemical Engineering, Vol. 135,* doi: 10.1016/j.compchemeng.2020.106769

**III.** Shavalieva, G., Kazepidis, P., Papadopoulos, A.I., Seferlis, P., Papadokonstantakis, S., 2020, Environmental, Health and Safety Assessment of Post-combustion $CO_2$ Capture Processes with Phase-change solvents. Submitted for publishing to *Sustainable Production & Consumption*.

**IV.** Shavalieva, G., Postacchini, P., Papadokonstantakis, S., 2020, Prediction of sustainability related properties: data science methods with incorporated prior knowledge, accepted for publication in *Proceedings of the 30th European Symposium on Computer Aided Chemical Engineering, Vol. 47, 1st Edition* (peer-reviewed).

**Authors' contributions**

Gulnara Shavalieva is the main author of **Papers I**, **III** and **IV**. She is a second author of **Paper II**. Her contribution is related to the development of the automated sustainability assessment procedure, its integration to computer-aided molecular design and writing the aspects of method and discussion related to the sustainability assessment. Associate Professor Stavros Papadokonstantakis was the supervisor of all the papers and has contributed with discussions and editing of all the papers. Principal Researcher Dr. Papadopoulos A.I. is the main supervisor of **Paper II** and has contributed to **Papers I** and **III** with flowsheets development and editing. Sara Badr has contributed to **Paper I** with editing and discussion. Professor Seferlis P. has contributed with discussions for **Paper I**. **Papers II** and **III.** Pietro Postacchini has contributed to **Paper IV** with method development and discussion.

Additional publications not included in the thesis:

- Shavalieva, G., Papadokonstantakis, S., Kazepidis, P., Papadopoulos, A.I., Seferlis, P., 2018, Sustainability analysis of phase-change solvents for post-combustion $CO_2$ capture, Chemical Engineering Transactions, Vol. 76 p. 1045-1050, doi: 10.3303/CET1976175

- Papadopoulos, A.I., Perdomo, F.A., Tzirakis, F., Shavalieva, G., Tsivintzelis, I.., Kazepidis, P., Nessi, E., Papadokonstantakis, S., Seferlis, P., Galindo, A., Jackson, G., Adjiman, C.S., 2020, Advanced Molecular Engineering of Efficient and Sustainable Phase-change Solvents for $CO_2$ capture. Submitted for publishing.

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Gulnara Shavalieva, Gothenburg, May 2020

# List of abbreviations

| | |
|---|---|
| AMP | 2-amino-2-methyl-1-propanol |
| BDA | 1,4-butanediamine |
| CAMD | Computer-aided molecular design |
| CCS | Carbon capture and storage |
| CED | Cumulative energy demand |
| DBA | Di-n-butylamine |
| DEEA | N,N-diethylethanolamine |
| DECA | N,N-Diethylcyclohexylamine |
| DETA | Diethylenetriamine |
| DMCA | Dimethylcyclohexylamine |
| DPA | Dipropylamine |
| ECA | N-ethylcyclohexylamine |
| EHS | Environment, health and safety |
| FF | Far field |
| GWP | Global warming potential |
| HEPTA | Heptanamine |
| HEX | Heat Exchanger |
| HEXA | Hexylamine |
| HSS | Heat stable salts |
| IDHL | Immediately dangerous to life or health |
| LCA | Life cycle analysis |
| MAPA | N-Methyl-1,3-diaminopropane |
| MCA | Methylcyclohexylamine |
| MEA | Monoethanolamine |
| MMEA | Monomethylethanolamine |
| MSDS | Material safety data sheet |
| NDELA | N-Nitrosodiethanolamine |
| NF | Near field |
| OEL | Occupational exposure limit |
| PEL | Permissible exposure limit |
| PoD | Potential of danger |
| RED | Relative energy difference |
| SBPA | N-sec-Butyl-n-propylamine |
| STEL | Short-term exposure |
| S1N | Cyclohexylpropane-1,3-diamine |
| TETA | Triethylene tetramine |
| TWA | Time-weighted average |

# Table of contents

# 1 Introduction

The year 2019 has been marked by unusually extreme weather and environmental disasters that cost billions of dollars in damage and resulted in loss of a vast area of forests and millions of living species. These disasters are most likely direct results of climate change, which are predicted to get worse if the society continues to follow the unsustainable path of development characterised by overdependence on fossil fuels resulting in high levels of carbon dioxide ($CO_2$) in the atmosphere. Climate models predict that the global surface temperature is likely to exceed 1.5-2°C above pre-industrial levels, if efficient decarbonization measures are not introduced by 2030[1]. Even 2°C increase in the temperature will have the catastrophic consequences like loss of the coral reefs, the Arctic sea ice, 20-40% of the Amazon forest and some islands[2], extinction of rare species, increase in frequency of floods, droughts and heatwaves[3], substantially lower crop yields[4], decrease in freshwater availability, elevated incidences of vector-borne diseases[5] and millions of climate refugees[6]. The decarbonization measures allowing drastic reduction of the emissions require shift in the way today's energy and industrial sectors, which are among the largest emitters of $CO_2$, are operated. Despite the positive changes in the energy sector due to a sharp decrease in the $CO_2$ emissions of developed countries (thanks to the growing share of renewable energy sources, higher nuclear output, and the reduced use of coal[7]), global $CO_2$ emissions levels are still rising. This demonstrates the need for increased mitigation efforts such as change in feedstock and increase in process efficiency. These, however, are not always technically or economically feasible[8].

Carbon capture and storage (CCS), including the combination of bioenergy with CCS (BECCS), can play a significant role in the rapid decarbonization of the power and industrial sectors[9]. Implemented at the energy and industrial plants emitting high amounts of greenhouse gases, CCS can mitigate 80-90% of the emissions of a single plant[10] without critical changes of the key aspects of the process. However, in spite of the potential to drastically reduce the process emissions, lack of regulatory frameworks and $CO_2$ infrastructure, public acceptance, and high costs associated with the capture technology hinder the near-term widespread adoption of the CCS[11].

Carbon capture by chemical absorption is the most mature and technically feasible carbon capture technology for near term implementation due to its potential to be retrofitted to existing industrial facilities[12]. It is state-of-the-art technology that is already in use by the carbon capture plants at commercial operation. However, a high energy penalty of the solvent regeneration, which is the main driver of the capture cost, stimulates search of alternative solvent options and different process designs with reduced energy demand[13]. It is reported that the energy requirement of solvent regeneration in the conventional systems could be decreased on average by 10 - 30%[14] by optimizing the process configuration alone. New solvent alternatives could reduce the energy requirement of the process even further, along with improving safety of the process which typically circulates a large amount of the solvent flow. An alternative to the conventional solvents (e.g. monoethanolamine (MEA), diethanolamine, piperazine) that has emerged in the past two decades are phase-change solvents which, under exposure to $CO_2$ and/or changes in process temperature, exhibit phase separation to $CO_2$ lean and $CO_2$ rich

phases. The lean phase is then recycled to the absorber, decreasing the amount of solvent sent for regeneration, cutting the energy requirement of the process and, thus, cost of the capture (e.g., up to 50% compared to MEA systems[15]). Furthermore, temperature-dependent or thermomorphic phase-change solvents may be regenerated at lower temperatures (<100°C) than the conventional alternatives, making it possible to utilize low value heat for the stripping process[16]. Examples of the phase-change solvents and their key performance and operational aspects are given in Table 1-1.

The benefits of the phase-change solvents in terms of energy are widely investigated, however, the human safety and environmental impacts associated with the new solvent behaviour and alternative energy system configuration during large-scale operation should also be evaluated to advance the technology to higher technological readiness level (TRL).

**Table 1-1: Examples of the phase-change solvents with key performance and operational aspects[15]**

| Solvent | Key performance aspects | Operational issues | TRL |
|---|---|---|---|
| DMCA/MCA/AMP (5.5 M, 3:1:1.5) | Regeneration energy: 2 GJ/ton $CO_2$ | Volatility losses, corrosion by MCA mainly | 3-4 |
| DMX-1 (blend) | Reboiler duty: 2.3-2.5 GJ/ton $CO_2$ | Foaming | 5 |
| DEEA/MAPA (5M, 2M) | Reboiler duty: 2.2-2.4 GJ/ton $CO_2$ | Volatile losses, corrosion similar to MEA | 5-6 |
| BDA/DEEA (2M, 4M) | - 46% higher cyclic loading than 5M MEA,<br>- 48% higher cyclic capacity than 5M MEA,<br>- 11% higher cyclic efficiency than 5M MEA. | - | 2-3 |
| TETA/ DEEA (5 mol/kg, 1:4) | - 40% higher cyclic loading capacity than MEA,<br>- 15% lower heat of absorption than MEA,<br>- 50% lower sensible heat than MEA,<br>- stripping heat 30% lower than MEA,<br>- overall energy requirements 30% lower than MEA. | - | 2-3 |
| DETA/ Sulfolane/ $H_2O$ (20 wt.%, wt. 40%, wt. 40%) | 35% higher cyclic loading than 30wt% MEA | - | 2-3 |

## 1.1 Aims and scope

The aim of this thesis is to promote selection of more sustainable solvent solutions for $CO_2$ capture by evaluation of the environmental, health, and safety aspects of a comparatively new class of solvents for $CO_2$ capture, phase-change solvents. The evaluation is done at different scales:

- substance level, where the feasibility of selection of more sustainable chemical structures during the computer-aided molecular (CAMD) design of solvents is investigated
- process level, where the assessment of the capture system utilising phase-change solvents is performed

In order to perform such an evaluation, the following issues were addressed:

- simultaneous computation of life cycle and environmental, health, and safety (EHS) impacts using an index-based sustainability framework within the CAMD procedure
- filling in data gaps existing for molecular properties required for computation of EHS indices
- assumptions and complementary modelling required for application of the combined life cycle analysis (LCA) and EHS hazard index-based framework for $CO_2$ capture process assessment

## 1.2 Outline of the thesis

The thesis covers the background and key findings of the four appended papers. Chapter 2 describes the phase-change solvents for $CO_2$ capture and their selection procedure. In addition, existing streamlined LCA and hazard assessment methods and process assessment of the conventional carbon capture systems are shortly discussed. Chapter 3 presents the methodology used for environmental, health, and safety assessment of phase-change molecules at substance and process levels. Main findings of the assessment are presented in Chapter 4. Conclusions are given in Chapter 5 and future work is introduced in Chapter 6.

In **Paper I**, a data science method based on similarity approach is described and tested to automatically predict molecular properties required to calculate EHS indices. The approach is then applied within the CAMD procedure when the EHS and LCA indices are computed during the molecular screening procedure to identify phase-change molecules that can be used as solvents for $CO_2$ capture. The integration and results of the simultaneous CAMD with sustainability assessment of the molecules are presented in **Paper II**.
**Paper III** describes the environmental, health, and safety aspects of the carbon capture systems that utilize selected phase-change solvents.
**Paper IV** introduces a potential way to gather prior information from scientific literature as a first step in development of hybrid prediction models, which, in the context of this thesis, refers to molecular properties predictive models complimented by prior knowledge existing in the

field. The need for the hybrid models was identified during the work described in Paper I and Paper II as a possible solution to such limitations as low accuracy and transparency of the predictive models and lack of data for training.
Connection between the papers is presented graphically in Figure 1-1.

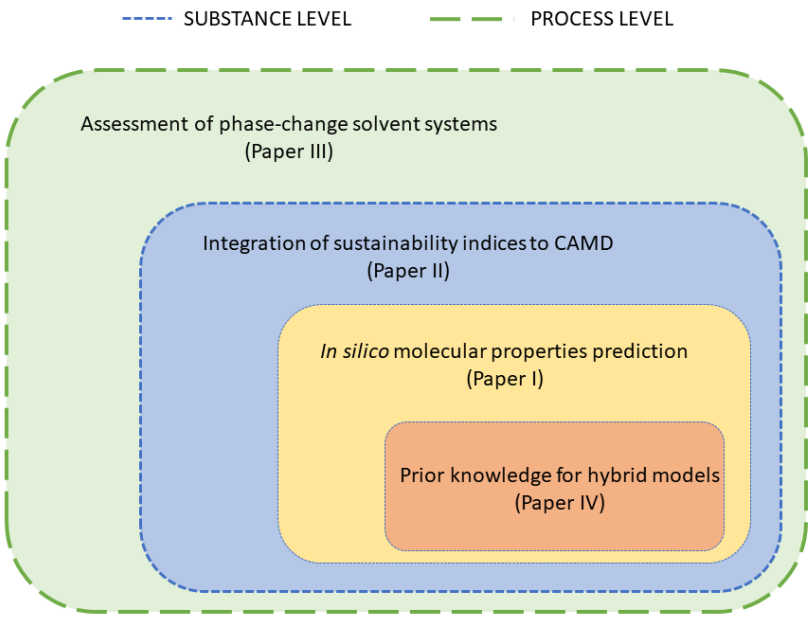



**Figure 1-1: Overview of the connections between the topics covered in the papers appended to this thesis**

# 2 Background

## 2.1 Phase-change solvents

The concept of phase-change solvents in the context of gas-liquid absorption was first patented by Liang Hu in 2005[17]. Later the concept has found application in $CO_2$ capture and has been attracting increased research interest as third-generation absorbents (second generation: demonstration in 2020–2025-time frame; third generation: at early development stage)[18] since then.

Phase-change or biphasic solvents are miscible solute-solvent mixtures undergoing a phase liquid-liquid or liquid-solid separation promoted by $CO_2$ absorption and/or alteration of temperature[19]. $CO_2$-triggered solvents generate two phases in result of changes in (i) polarity, called switchable polarity solvents, (ii) ionic strength, named switchable water solvents, or (iii) hydrophilicity when the solute reacts with the $CO_2$. Switchable polarity solvents are usually nonaqueous mixtures. Reversible switch of low to high polarity after the $CO_2$ absorption results in change of solubility of solutes in solvents and thus, separation of phases. The phase separation in switchable water solvents occurs when an ionogen compound of an aqueous mixture becomes ionic under dissolution of $CO_2$ in water. As a result, the homogeneous mixture of a low ionic strength is transformed to a solution of bicarbonate salt with increased ionic strength leading to a liquid-liquid phase separation[19]. Switchable hydrophilicity solvents are hydrophobic liquids having little miscibility with water before they are exposed to $CO_2$. Absorption of carbon dioxide makes the solvent hydrophilic and completely miscible with water[20], the desorption of $CO_2$ leads to separation of phases. Among $CO_2$ triggered solvent mixtures suitable for $CO_2$ capture are both nonaqueous, (i.e., amine-alcohol, amino acid-alcohol, ionic liquid-amino acid blends), and aqueous (i.e., water-amines mixtures or solutions of salts of amino acids[19]).

Solvent phase separation triggered by changes in temperature (referring to so called thermomorphic solvents) normally includes mixtures of lipophilic amines and water. Phase separation in such mixtures happens when the increase in the process temperature breaks the intermolecular hydrogen bonds between amine and water[19].

Nonaqueous solvents have lower regeneration temperature compared to the aqueous solvents due to replacement of water with organic solubilizers or ionic liquids. This is beneficial in terms of solvent degradation and evaporation, corrosiveness, and heat requirements for solvent regeneration. However, practical application of the nonaqueous solvents might be restricted because of the presence of water in the flue gas coming for treatment. The presence of water might affect the efficiency of the process, introducing the need for additional measures for water management[19]. However, $CO_2$ capture with nonaqueous solvents has not yet been fully assessed and requires more research. Aqueous solvents capture processes have been studied to a larger extent, some aqueous phase-change solvents reaching technology readiness levels of 4 and 5[15]. Table 2-1 gives examples of phase-changed solvents and drivers for their phase separation.

Solvent blends (e.g., salts of amino acids) resulting in solid $CO_2$ rich phase, might create process challenges due to precipitation, while the blends exhibiting liquid-liquid separation are easily incorporated to the existing absorption/desorption systems though the addition of the mechanical separation step[15]. (See Figure 2-1). Possibly, due to this reason, most of the phase-change solvents introduced as $CO_2$ capture solvents, and also investigated in this work, are solvents exhibiting liquid-liquid phase separation.

**Table 2-1: Examples of phase-change solvents with various phase separation drivers**

| Solvent | Phases | Phase separation driver |
|---|---|---|
| $CO_2$-triggered | | |
| Dipropylamine (DPA) | Liquid-solid | Change in the polarity[21] |
| MEA/isooctanol | Liquid-liquid | Change in the polarity[19] |
| Tetrabutylphosphonium N-trifluoromethanesulfonylleucine (ionic liquid)/water | Liquid-liquid | Change in the hydrophilicity[20] |
| N-methyldiethanolamine /water | Liquid-liquid | Change in the ionic strength (switchable water)[20] |
| Potassium taurate (amino acid salt) / water | Liquid-solid | Change in the polarity[19] |
| MAPA/DEEA/water | Liquid-liquid | Change in the ionic strength (switchable water)[20] |
| Thermomorphic | | |
| DPA/DMCA /water | Liquid-liquid | Change in miscibility triggered by the temperature change[19] |
| DMX solvent | Liquid-liquid | |
| MCA/DMCA/AMP | Liquid-liquid | |

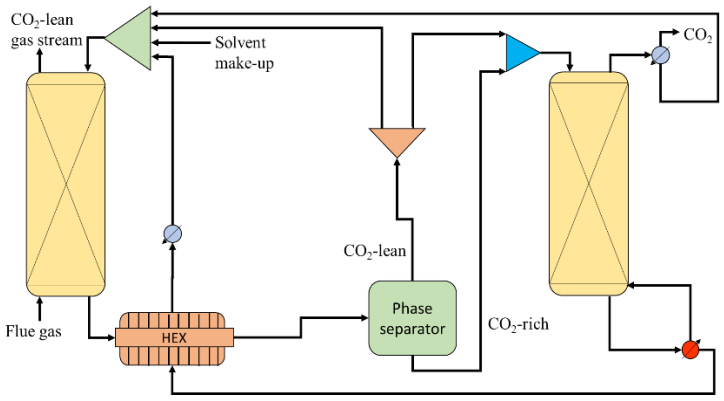



**Figure 2-1: $CO_2$ capture with phase-change solvents[22]**

## 2.2 Screening and selection of phase-change solvents via CAMD

The selection of solvents exhibiting liquid-liquid phase-separation is not a trivial task due to the extensive number of potential options and very non-ideal interaction between solvent molecules, water and $CO_2$. The majority of phase-change solvents reported in the literature are based on experimental screening[23–28] with criteria like absorption and cyclic capacity, reaction rate, presence of phase separation, no precipitation, salt or gel formation[16]. Despite the necessity of experimental testing, experimental screening of the vast number of candidates is a rather expensive procedure in terms of effort and cost. Furthermore, there is a high chance of overseeing many molecules with the beneficial performance due to the unfeasibility of testing every molecular structure, especially if the molecules are generated through an automated procedure of computer-aided molecular design (CAMD). The combination of knowledge obtained during the experiments with CAMD allows investigation of an enormous range of structures with the selection of the most promising candidates, which are then tested experimentally in order to verify the results.

CAMD is a method with numerous prior implementations in the design of solvents, polymers, heat exchange fluids, biofuel additives, etc[29]. CAMD has also been previously used for identification of conventional (non phase-change) $CO_2$ capture solvents[30]. The method enables the reverse engineering of molecular structures, in order to identify the one(s) that exhibit optimum performance based on a set of desired criteria. The desired set of properties is calculated for the chemically feasible molecular structures generated from a set of building blocks or molecular fragments[31], also called molecular descriptors. Chemically feasible molecular structures are CAMD solutions that do not break any inherent laws of chemical bonding. Furthermore, constraints can be added to eliminate certain structural features (e.g., N-N connections) from the solution space or guarantee the number of their appearance in the produced molecular structures[32]. Based on the given molecular fragments (e.g., functional groups like $CH_3$-, $CH_2$-, OH-, $NH_2$-, NH-) CAMD finds optimal or near optimal molecular structures that meet the desired performance criteria for the investigated application, for example, carbon capture. The desired criteria for identification of carbon capture solvent alternatives include molecular properties like density, vapour pressure, heat capacity, viscosity and relative energy difference (RED) set as objective functions. The solvent density defines solvent volumetric flow rate used for the carbon separation, and thus, size of the equipment and pumping power. The solvent vapor pressure indicates the potential for volatile losses of the solvent. The heat capacity is related to sensible heat requirements for the process. The viscosity parameter affects the mass transfer in the packing materials of the columns while RED can be used as an index for the solubility of the solvent towards $CO_2$. Identification of the preferable molecular structures requires maximization of the molecular density value and minimization of all the other objective functions. The molecules exhibiting phase-change phenomena are identified by adding extra criteria, namely the Hansen solubility parameters of the solvent, water, and $CO_2$. Setting the difference between the Hansen solubility parameters of solvent and water solubility parameters above a threshold value $\varepsilon$ at desorption temperature and the difference between the Hansen solubility parameters of solvent and $CO_2$ below $\varepsilon$ at absorption

temperature enables identification of solvent molecules with less affinity with water at desorption conditions and more affinity with $CO_2$ at absorption conditions[33]. More selectivity criteria can be added to the procedure. However, it is important that all the property criteria used within the CAMD are readily calculated by, for example, group contribution (GC) methods or algebraic equations, since this type of calculation is going to be performed at every iteration of the CAMD optimisation algorithm. The molecular structures are given as a set of functional groups (molecular fragments) and number of appearances of each group in the structure. This type of description of molecular structures is compatible with GC methods and also the basis for the methods used for estimating the properties appearing in the objective function. All the feasible molecular structures are then optimized against the desired criteria via multi-objective optimisation using the concept of Pareto fronts[34] and Simulated annealing algorithm[35] for solving the optimisation problem.

## 2.3 Streamlining LCA and hazard assessment for solvent design

From early on, it has been realized that it is important also to account for the environmental, health, and safety aspects within the CAMD procedure. Early evaluation of the impacts associated with the production and use of hazardous chemicals in the industrial process could enable their replacement with more benign alternatives, which would minimize harmful impact to human health, and the environment. However, even automated solvent design combined with the experimental testing might still result in high cost in terms of materials and effort. Quick evaluation of the environmental, health, and safety aspects of the solvent candidates early during the solvent design might help to reallocate resources and effort away from the candidates demonstrating negative environmental or safety concerns[36]. Thus, there is a growing interest in development of quicker, more streamlined assessment methods to obtain a first indication of the potential impact already at the solvent design stage.

Various Quantitative Structure-Activity Relationship (QSAR) models, GC methods for example, correlating a numerical description of molecular structure to known biological activity[37] for various EHS related properties (e.g. toxicity, bioconcentration) have been developing over many years. Over the last few years effort has been made to create automated methods to additionally estimate the life cycle impacts in different categories applying methods of data science. The first automated LCA impact methods are those of Wernet et al. (2008, 2009) who used neural networks and principal component analysis based on molecular descriptors[38,39]. More recent studies propose the improved version of the same approach by selecting different molecular descriptors and neural network structures[40], including thermodynamic and other parameters[41].

However, while there are a number of CAMD studies incorporating EHS indicators[42–45], there are limited numbers of works considering the LCA impact constraints. For instance, the work by Mehrkesh and Karunanithi (2014)[46] included downstream LCA impacts associated with the emissions of the chemicals. Heintz et al. (2014)[47] and Weis and Visco (2010)[48] used a single LCA score estimated on the basis of quantitative-structure property relationships (QSPRs) built on available data for 46 frequently used solvents. The main challenge of

incorporation of more recent streamlined LCA methods lies in the lack of models that can be easily incorporated to the CAMD framework within a short time.

## 2.4 Process assessment of the conventional capture systems

The environmental and health aspects of the capture processes with conventional solvent capture systems (e.g., based on MEA) are reported in numerous studies. While most of the studies focus on the energetic performance of the capture system[49], some studies focus on the emissions associated with the amine-based capture systems[50–53], and others assess and explain solvent behavior in the system resulting in undesired impact to health and environment[54–56]. Life cycle studies typically report the effect of the carbon capture and CCS to the performance of power plants[57–59]. The majority of studies cover the MEA-based systems (with a few exceptions) for other solvents[60–63].

The importance of a more holistic LCA approach in evaluating the environmental impact of CCS systems is highlighted by Sathre et al. (2012)[64] who advocates for a system-wide level assessment including the scale-up challenges, non-climate environmental impacts, and uncertainty management by a comprehensive scenario analysis. A framework applying both LCA and EHS assessment is proposed by Badr et al. (2017)[60], who indicates the need for a comprehensive assessment combining safety, health, and environmental hazard analysis with more traditional performance indicators such as LCA and cost factors. The influence of the change in the process operating conditions to the overall impact of the system is also emphasized[60].

# 3 Methodology

In this work, the impact of phase-change solvents and phase-change solvent capture systems was evaluated by a combined life cycle (LCA) and environmental, health and safety hazard assessment (EHS). The assessment was performed at substance level (when the sustainability indicators are added into the CAMD) and at process level (when the impact of the usage of phase-change solvents in the carbon capture plants is evaluated).

## 3.1 Substance level

Substance level assessment is required to identify molecules with lower environmental, health, and safety impact during the CAMD and selection of potential phase-change solvents for $CO_2$ capture. In order to assess the impact of the molecules generated in CAMD, LCA and environment (E), health (H), and safety (S) hazard assessment indices were computed for all the molecular alternatives in each iteration of the CAMD optimisation procedure and, together with the other CAMD constraints and molecular properties, were used to calculate the objective function. This "on-line calculation" relies on the availability of empirical and analytical predictive models for all the molecular properties included in the computation of the indices, and thus no data gaps were allowed.

The integration of the LCA and E, H and S indices calculation procedure to CAMD is shown in Figure 3-1.

The multicriteria solvent design problem (CAMD) was formulated by set of objective functions (Eq.1)[33]:

$$\begin{aligned} &\max_{M\in G} \quad \rho \\ &\min_{M\in G} \quad P_{vp}, C_p, n, RED, GWP, CED, EI99, S, H, E \\ &\text{s.t.} \quad T_m^{Abs} \\ &\qquad T_{bp} \geq T_{Des} \\ &\qquad |\delta^s - \delta^{H_2O}|_{T_{Des}} \geq \varepsilon \\ &\qquad |\delta^s - \delta^{CO_2}|_{T_{Abs}} \leq \varepsilon \end{aligned} \tag{1}$$

where $\rho$ is solvent density, $P_{vp}$ is solvent vapour pressure, $C_p$ is solvent heat capacity, $n$ is solvent viscosity, *RED* is the relative energy difference index calculated on the basis of Hansen solubility parameter (δ) between the solvent and $CO_2$, minimization of RED allows identification of solvents with high solubility toward $CO_2$. $T_m$ is the melting temperature of the solvent, $T_{bp}$ is the boiling point of the solvent, $T_{Abs}$ is the absorber temperature set to 40°C, $T_{Des}$ is the desorber temperature set to 90°C, $\delta^s$ is the Hanson solubility parameters of solvent, $\delta^{H_2O}$ is the Hanson solubility parameter of water, $\delta^{CO_2}$ is the Hanson solubility parameter of $CO_2$, $\varepsilon$ is the threshold value set to 7 $(MPa)^{0.5}$ (based on a rule of thumb stating that below this value a solute is miscible in a solvent), GWP, CED, and EI99 are the global warming potential, the cumulative energy demand, and the Eco-indicator 99 calculated as cradle-to-gate life cycle impact assessment metrics for the solvent production, and E, H, and S are the indices for the

environmental, health, and safety hazard assessment of the solvent; the LCA and hazard assessment metrics are also called "sustainability framework" in this work.

The molecules were presented as a set of functional groups with the number of their appearance in the molecules. The following functional groups are considered in this work: $CH_3$, $CH_2$, CH, C, OH, $CH_2NH_2$, $CH_2NH$, $CH_2N$, $CHNH_2$, CHNH, $CH_3NH$, $CH_3N$. For example [$CH_3$, $CH_2$, $CH_2NH_2$] [1,4,1]. The number of functional groups appearance in each molecule ranged from 6 to 16, up to 1 amine group was allowed in each functional group. The latter allows generation of simpler molecules, with fewer isomers, making it easier to interpret the results. In order to include trade-offs between all the objective functions in a set of "optimal" solutions, the results of solving the optimisation of the multi-objective problem were obtained in the form of 11 dimensional Pareto fronts. In order to perform comparisons and visualize the results in the form of 2 dimensional Pareto fronts, an aggregated index between the index and each property was calculated by Eq.(2)[33] after the optimization algorithm was terminated.

$$\min_{i \in SI} J_i = \sum_{j \in Pr} a_{i,j} \cdot x^*_{i,j} \tag{2}$$

where $x^*_{i,j}$ is the scaled property considered (i.e., $j$ refers to one of $\rho, P_{vp}, C_p, n, RED, GWP, CED, EI99, S, H, E$) for a molecular structure $i$, and $a_{i,j}$ represents a unity coefficient that is positive for properties that need to be minimized and negative for those to be maximized. The scaling factor was obtained via a standardization method presented by Eq.(3):

$$x^*_{i,j} = \frac{x_{i,j} - \mu_j^{SI}}{st_j^{SI}} \tag{3}$$

where $x_{i,j}$ represents the original value of the property $j$ for molecule $i$, $\mu_j^{SI}$ and $st_j^{SI}$ are the mean and standard deviation of the considered property, calculated over the entire set of molecular structures in a vector *SI* containing the resulting Pareto fronts. To visualise and interpret the multi-objective optimisation result Pareto fronts were studied per property $j \in Pr$ and index $J$ for every $i \in SI$.

All the details of the integration procedure can be found in Paper II.

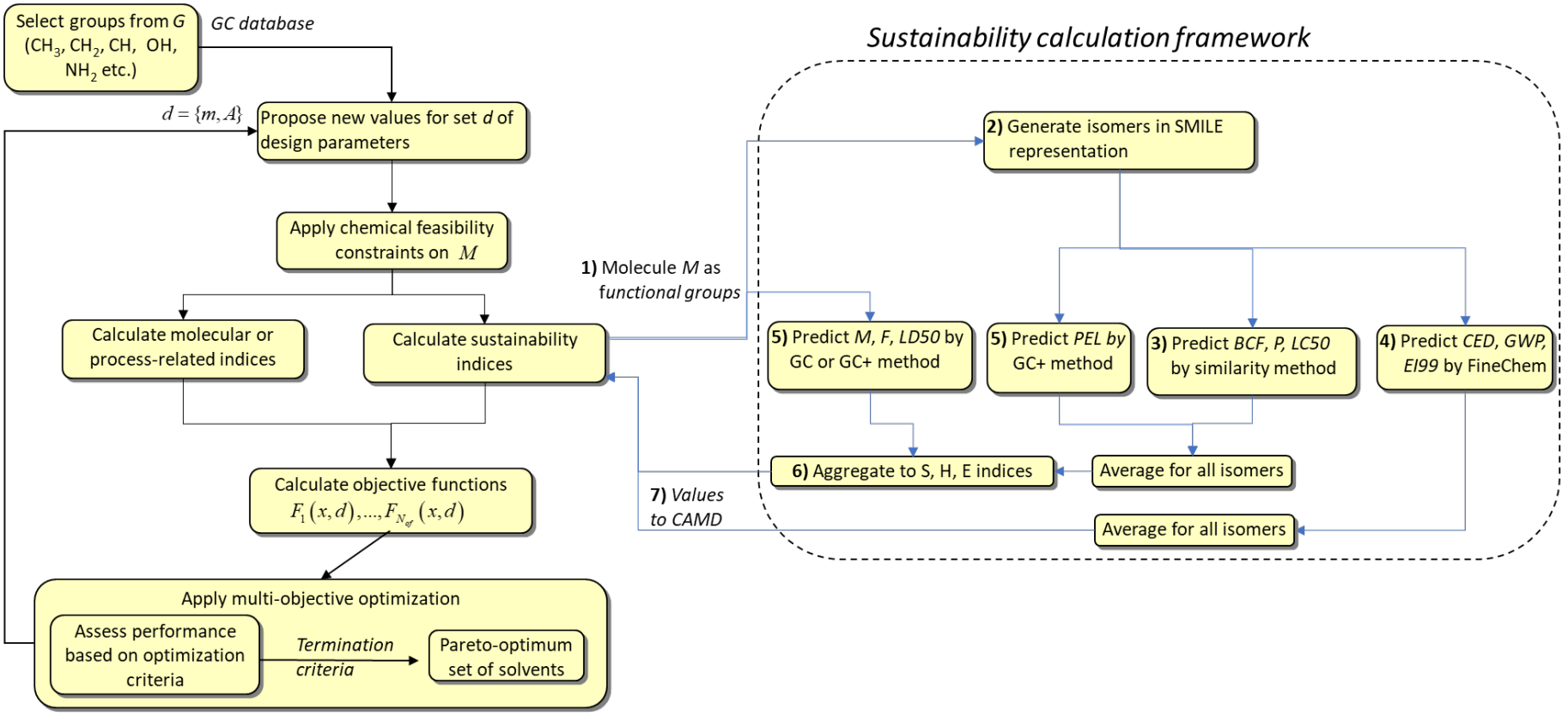



**Figure 3-1: Simultaneous CAMD and sustainability assessment calculation step. Source: Paper II**

### 3.1.1 LCA indices

Within the CAMD, the LCA indices were calculated automatically by streamlined FineChem models[39] estimating the environmental impact of producing the solvent based on its molecular structure. The phase-change molecules are not yet produced or used at large scale and are missing from the LCA inventory databases. The FineChem models estimated LCA impact associated with the production of 1 kg of a substance. The "cradle-to-gate" boundaries were used to consider the production process of the substance itself as well as production of material and energy applied during the process. The FineChem models rely on industrial production data complemented by background data inputs from Ecoinvent[39]. Global warming potential (GWP 100a)[65], cumulative energy demand (CED) and an endpoint of Eco-indicator 99 (EI99) impact assessment method[66] were selected; these LCA metrics have been shown to be predicted more accurately by the FineChem.

The FineChem models use information on a number of molecular features obtained from a SMILE (Simplified Molecular Input Line Entry Specification) form of molecular alternatives generated in CAMD. These molecular features are[39]:

- molecular weight
- number of functional groups (total)
- number of oxygen atoms in keto and aldehyde groups
- number of oxygen atoms not in keto and aldehyde groups
- number of nitrogen atoms
- number of halogen atoms
- number of aromatic or aliphatic rings
- number of ternary or quaternary carbon atoms
- number of heteroatoms in rings
- number of unique substitutes on aromatic rings

The SMILEs were formed for all the possible isomers of a molecule given as a set of functional groups and the number of their appearance obtained from the CAMD (See Figure 3-1). Thus, the isomers of the same molecule can have different LCA values. Some of the isomers can have a ternary carbon for example, leading to an increased impact of the production of such a molecular structure. The final LCA indices returned to the main algorithm were average values between all the isomers generated for a molecule (a set of functional groups).

### 3.1.2 EHS indices

E, H, and S indices are based on dangerous properties, parameters and molecular properties summarized in Table 3-1. The environmental (E) aspect evaluates potential damage to the environment caused if a solvent molecule is released to the environment as a result of everyday operation or accidents. The health (H) aspect assesses the influence of everyday contact with chemicals to the health of workers. The safety (S) aspect gives an indication of the hazards associated with the use of a solvent in the process, its potential to lead to accidents and its short-term effects to plant workers.

In order to calculate single E, H, and S scores, various dangerous properties should be computed for every molecular alternative. The dangerous properties are based on certain parameters or molecular properties (See Table 3-1). S score is based on three dangerous properties: mobility, flammability/explosiveness and acute toxicity. H score is estimated by the chronic toxicity property. E score is estimated by water mediated effects, degradation, air mediated effects and accumulation properties[67]. The E, H, and S indices were calculated based on an index (*I*) taking value between 0 and 1 depending on the value of a certain dangerous property. Figure 3-2 presents an example of the index-dangerous property parameter scale for the acute toxicity. Scales for the parameters were obtained from work of Koller (2000)[67] and Badr (2016)[68]. The final scores were computed by Eq. (4):

$$Score_i = \sum_{j=1}^{n} I_{i,j} \quad (4)$$

where $Score_i$ is the E, H or S of substance; $I_{i,j} = I_{i,j} + F_{i,j}$ – is a dangerous property index in the corresponding hazard category modified by a fate index (*F*) according to Koller (2000)[67]. The fate index is a function of molecule volatility and persistence in the environment; the higher the volatility and persistence of the substance, the higher the risk of the molecule to cause an undesired effect [68]. *n* – represents the number of dangerous properties considered in the category E, H, or S.

**Table 3-1:Dangerous properties for EHS hazard assessment and their estimation methods** [33]

| Dangerous Property | Parameter/Molecular property | On-line estimation method |
|---|---|---|
| | **Safety (S)** | |
| Mobility | Difference between boiling point of the pure substance and highest process temperature | Group contribution [69] |
| Flammability/ Explosiveness | Difference between the flashpoint of the pure substance and the highest process temperature | Group contribution[69] |
| Acute toxicity | *LD50* (rat) – the amount of orally ingested chemical that causes death to 50% of rats (mg/kg body weight) | Group contribution+ [70] |
| | **Health (H)** | |
| Chronic toxicity | Permissible exposure level (*PEL*) – a US legal exposure limit ($mg/m^3$) of an employee to a chemical, given as the average exposure concentration over 8 hours | Group contribution +[70] |

| Environment (E) | | |
|---|---|---|
| Water Mediated Effects | Toxicity ($LC50_{aq}$) – concentration (mg/l) of a chemical in water that causes death/effect to 50% of most sensitive aquatic species | Similarity [71,72] |
| Degradation in the environment | Persistency (*P*) (in days) represents half-life of a chemical in the environment | Similarity [71,72] |
| Air Mediated Effects | Chronic toxicity index calculated based on permissible exposure limit (*PEL)* | Group contribution +[70] |
| Accumulation | Bioconcentration factor (*BCF*) assesses accumulation of a chemical in a living organism. Calculated as concentration of the chemical in an aquatic organism divided by the concentration in the water. | Similarity [71,72] |

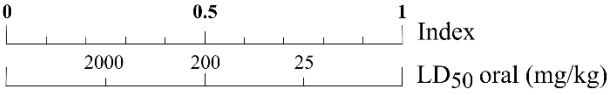



**Figure 3-2: Acute toxicity index calculation based on LD50 oral value**

## 3.1.3 Estimation methods of EHS molecular properties for use in CAMD

*Group contribution methods*

Group contribution (GC) methods are empirical approaches for estimation of molecular properties (e.g. boiling point, solubility) based on molecular groups constituting the molecule. The methods follow the so-called "additive principle", in which the molecular property value is obtained by summing up contributions of all the molecular groups[73]. The contributions of single molecular groups are estimated from the available data on many molecules obtained via *in vitro* or *in vivo* experiments. The GC methods provide estimations based entirely on the structure of a molecule giving quick results without requiring substantial computational time[70]. However, there are several cases where group contributions-based models are not available due to the lack of experimental data for a sufficient number of molecules to determine all individual group contributions. In such cases, the missing contributions are computed with the help of additional models such as atom connectivity index (CI), performing estimations using single atoms and valence connectivity indices[74]. The combined GC and CI approach is known as the group-contribution+ (GC+) presented by the Eq. (5)[70]:

$$f(X) = \sum_i N_i C_i + f(X^*) \quad (5)$$

where X is the molecular property parameter, $C_i$ is the contribution of the molecular group of type $i$ that occurs $N_i$ times, and $f(X^*)$ is the missing group contribution computed by the CI method according to Eq. (6) and Eq.(7)[70,74]:

$$f(X^*) = (\sum_m n_m f(X_m)) + d \quad (6)$$

$$f(X_m) = \sum_j a_{m,j} A_{m,j} + b({}^v\chi^0)_m + 2c({}^v\chi^1)_m \quad (7)$$

where $m$ counts the number of missing groups, $n_m$ is the number of times the $m$ missing group appears in the molecule, $a_{m,j}$ is the contribution of atom of type $j$ that occurs $A_m$, times in the $m$ missing group , ${}^{v}\chi^{0}$ is the zeroth-order (atom) valence connectivity index, ${}^{v}\chi^{1}$ is the first order (bond) valence connectivity index, $b$ and $c$ are adjustable parameters and $d$ is a constant for a specific molecular property. $a,b,c,d$ values, atom and bond connectivities and other values required for the computation can be found in original publication by Gani et al. (2005)[74].

*Similarity approaches based on data science*

The prediction capacity of GC methods is enough for estimation of the thermodynamic properties such as boiling or flash point, but there is still room for improvement of GC and other quantitative-structure property relationships (QSPR) models for predicting the molecular parameters associated with the LCA and EHS assessment. The prediction models applying recent methods of data science (mostly machine learning) reported improved accuracy of prediction[75,76].

The similarity approach applied for the prediction of selected molecular properties from Table 3-1 is using the kNN (k-nearest neighbours) supervised machine learning (ML) algorithm. The approach allows estimation of a missing property value using the most structurally similar molecules (nearest neighbours) with known property values. The estimation is performed by Eq. (8)[72,77]:

$$y_{pre,i} = \sum_{l=1}^{k} \frac{S_{i,l}}{\sum_{j=1}^{k} S_{i,j}} * y_{l,db} \quad (8)$$

where $y_{pre,i}$ is desired to predict property of molecule $i$. The $S_{i,l}$ is a similarity value between molecule $i$ for which property predictions are sought and a molecule $l$, found in a database, for which the desired property value $y_{l,db}$ is available, and $k$ is the optimal number of the similar neighbours used in the prediction found by a cross validation procedure (13, 4 and 9 for *BCF*, $LC50_{aq}$ and *P*, respectively). The similarity value is established by a Tanimoto coefficient, computed by Eq. (9):

$$S_{i,l} = \frac{c_{i,l}}{a_i + b_l - c_{i,l}} \quad (9)$$

where $a_i$ and $b_l$ are unique features of molecules $i$ and $l$, whereas $c_{i,l}$ is the number of molecular features which are common between the two molecules. The following molecular features were considered: hydrogen bond donor, hydrogen bond acceptor, basicity, acidity, aromatic ring, and halogens (F, Cl, Br, I)[78]. The features were encoded in the form of a molecular fingerprint and computed. The Tanimoto coefficient was computed with the help of an open source cheminformatics toolkit RDKit[78].

The database employed in the *BCF*, $LC50_{aq}$ and *P* property estimation procedure contained 2 016 structurally similar molecules with known property values. The database was generated from a more comprehensive database of Strempel (2012)[79] that has been reduced to contain only the compounds relevant to the $CO_2$ capture case, i.e. formed by the same functional groups used in the CAMD algorithm. The original database has 94 483 chemicals with either experimental or estimated PBT (persistency, bioconcentration, toxicity) data.

The detailed description of the method is given in Paper I and Paper II.

*Hybrid prediction models*

The ML models demonstrate improvement of the performance but often are black box models that are difficult to interpret[75]. Furthermore, the ML models rely on extensive sets of experimental data which might be limited for some molecular properties, for example permissible exposure levels, acute toxicity dermal, persistency, acidification potential, and global warming). Experimental data on safety of the chemicals is traditionally performed on living organisms, and an extensive experimentation is not acceptable, neither from an economical nor an ethical point of view. In fact, EU legislation encourages the development and use of alternative *in vitro* or *in silico* approaches to replace cruel animal testing[80].

One of the ways to address these limitations is to generate hybrid models by incorporation to a model knowledge existing in the field (i.e., prior knowledge). The prior knowledge can refer to data labelling, generic conclusions, functional trends between target and predictor variables, simplified input/output models for specific classes of chemicals, etc. The approach has been successfully applied in various fields, for instance, medicine[81], drug safety[82], materials[83], image recognition[84], but has not yet been applied for the molecular properties of interest for LCA and EHS assessment. One of the main reasons is that prior knowledge is not systematically extracted, classified and formulated in a way that can be effectively used for hybrid modelling. An approach for this first step of knowledge extraction for development of hybrid prediction models is shown in Figure 3-3 and described in Paper IV. The knowledge is extracted from research publications by means of natural language processing, resulting in a set of sentences of various forms (e.g., *There is a linear relationship between both acute and chronic toxicities and LogKow, suggesting that with the increase of hydrophobicity the aquatic toxicity increases*; *Aldehydes, alcohols and acids, as well as the parabens used as preservatives, are readily biodegradable and present moderate toxicity to aquatic life*) to be considered for development of hybrid models.

The hybrid models could be useful for safety evaluation of molecules without experimental data or in CAMD procedure, where the safety evaluation should be performed simultaneously with other constraints and estimation of objectives in all iterations of the optimisation procedure used for the design of the optimal candidates for various applications. Prior knowledge could improve the prediction capacity of ML models, for example, in the similarity type of models described above, by providing support in selection of the closest neighbours used in the prediction. The identification of the closest neighbours, or the most similar molecules, might be determined by the specific molecular features influencing the property value rather than the general structural similarity between the molecules. In other words, some of the molecular fragments might have a higher influence on the value of the specific property and, thus, should be prioritized when selecting the most similar neighbours for the prediction.

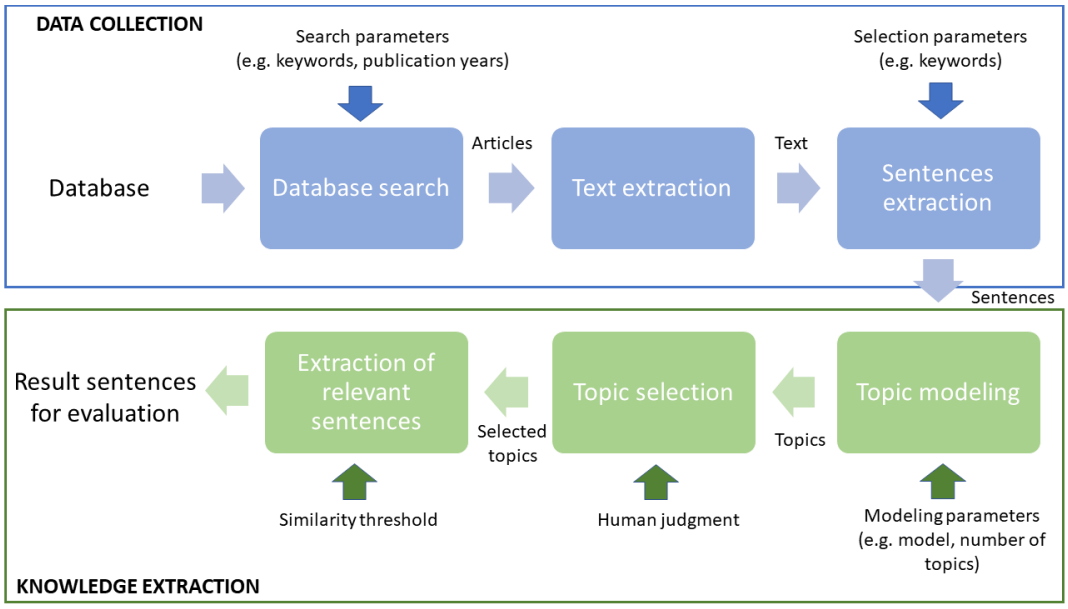



**Figure 3-3: Schematic representation of knowledge extraction procedure. Adapted from Paper IV**

## 3.2 Process level

Process level assessment evaluates the impact of the phase-change carbon capture systems. The assessment was performed by means of LCA and EHS supplemented by an exposure analysis. The method included evaluation of the extent to which problems typical for the conventional carbon capture systems might appear in the new phase-change system, as well as some additional process specific features of the phase-change systems. The problems might be associated with the molecular structure of phase-change solvents, quality of the feed flue gas and process design of the phase-change capture system. Such an analysis was required to introduce necessary mitigation equipment and improve the process design. The LCA and EHS assessment was then used to evaluate if the improved system could still potentially pose harm to the plant workers and environment and which aspects of the system might require particular attention[22]. Figure 3-4 shows the process structure after the introduction of the necessary mitigation equipment and scope for LCA and EHS assessment.

Under process conditions, solvent molecules tend to react with species other than $CO_2$ ($NO_x$, $SO_x$, $O_2$, soot), entering the system with the flue gas. As a result of the amines', used as a solvent, reaction with $NO_x$, substances, for example, carcinogenic nitrosamines, might be formed. Even low concentrations of nitrosamines in the air, 2.39-7.55 mg/m$^3$ [68] , are harmful to human health. The amounts of $SO_x$ and soot affect the amount of emissions from the capture system. Thus, if a flue gas coming into the capture unit contains high levels of $NO_x$ and $SO_x$, a flue gas pre-treatment (e.g., $NO_x$/$SO_x$ scrubber) might be needed. Oxygen and high temperature of the solvent regeneration process as well as the molecular structure of the solvent influence the degradation of the solvent molecules. In order to prevent the accumulation of the degradation products in the system, reclaiming is required. Washing sections are needed to remove the volatile degradation products and emissions of the solvent carried by the treated

flue gas leaving the absorber, The washing section and reclaimer waste flows are sent to the wastewater treatment unit, estimated by wastewater treatment models[85]. The solvent lost during the process needs to be constantly compensated for, increasing the solvent production.

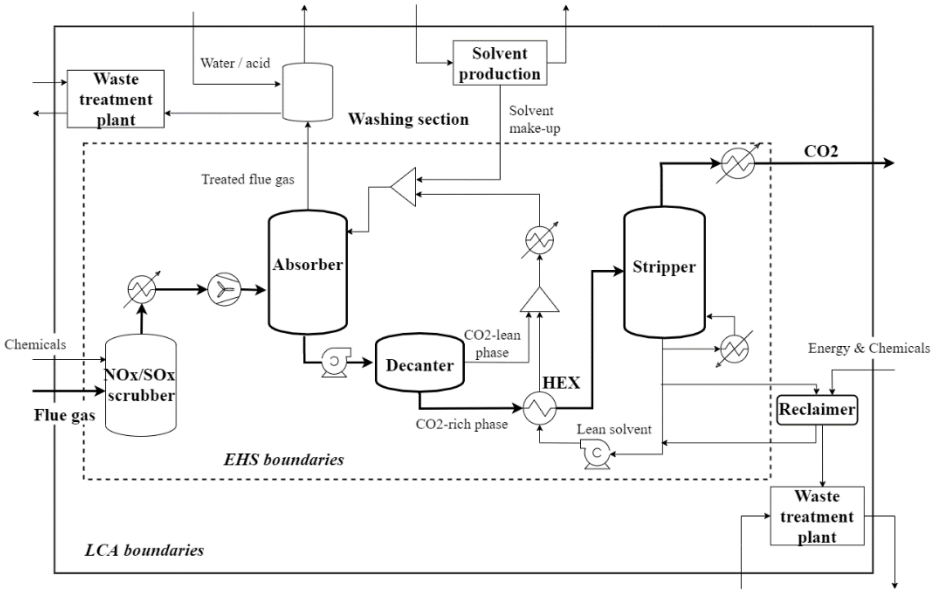



**Figure 3-4 Process structure and scope for LCA and EHS assessment of the carbon capture with solvent exhibiting liquid-liquid phase separation. Note that depending on the type of the phase-change solvent the position of the HEX might be before or after the decanter. Source: Paper III.**

### 3.2.1 LCA assessment

The aim of the process level LCA was to evaluate the impact of capturing 1 tonne of $CO_2$ (90% capture rate, 98% purity by mole) by a capture system using phase-change solvents at steady state process operation. It was also intended to compare the results with similar studies for conventional solvents (i.e., MEA). The system boundary was cradle-to-gate, including only impacts from chemical auxiliaries and energy utilities that are solvent or process dependent. Energy required to transport $CO_2$ containing flue gas to the capture site and compression and transportation of the captured $CO_2$ for further use or storage were excluded. Delivering the flue gas to the capture site is not expected to be dependent on the type of the solvent or process, and thus was assumed to be the same for all the solvent based capture systems. Compression of $CO_2$ for storage or utilization is mostly determined by the mode of transportation or usage, and was therefore, also assumed not to rely on the process or a solvent type if the solvent itself does not require specific process conditions (high pressure in the absorber or stripper, for example). Background data in the form of inventories for the production of chemical auxiliaries and energy utilities were taken from Ecoinvent 3.4[86]. The foreground data (i.e., process inventory data) were derived from process flowsheets created with the use of experimentally derived equilibrium data.

The following impact categories were considered for a life cycle impact assessment: global warming potential (GWP 100a), cumulative energy demand (CED) and a single score of

the ReCiPe-2008 method based on the hierarchist weighting scheme (ReCiPe)[87]. The selection of the impact categories used in the assessment was defined by the limited number of the impacts estimated by the FineChem models for the solvent production process. However, the more recent damage-oriented method ReCiPe was taken instead of EI99 compared to the substance assessment level. The ReCiPe score for the solvent production was calculated on the basis of correlation with EI99[88] computed by the FineChem. The correlation was developed after the CAMD results were obtained, thus, only EI99 was used at the substance level assessment.

More information on the elements of the procedure and the data considered in the LCA calculations can be found in the Supplementary material of Paper III.

### 3.2.2 EHS assessment

The EHS process level assessment took into consideration not only the inherent properties of the solvent molecule and other chemicals used in the capture system but also their corresponding flows and hold-ups in the process equipment. The dangerous properties in this case were computed on the basis of the material data sheets (MSDS) and other sources stating the experimentally obtained data on properties of the chemicals, if available. The missing properties were estimated by the on-line methods used during the substance level assessment. Aggregated E, H and S scores during the process level assessment were computed to be further combined with other sustainability indices during decision making. Total E, H, and S scores were calculated by Eq. (10) – (12).

$$S = \sum_{iS} max_F \left[\sum_j m_j^F \, I_j^{iS}\right] \tag{10}$$

where $m_j^F$ is the mass flow of a specific substance *j* in stream *F* of the $CO_2$ capture process system per kg of $CO_2$ captured under the same conditions as in LCA (e.g., 90% recovery and 98% mole purity); $I_j^{iS}$ is an index of substance *j* for dangerous property *i* in the safety category.

$$H = \sum_H max_j \left(m_j^1 I_j^H\right) \tag{11}$$

where $m_j^1$ represents 1 kg of chemical substance *j*. The amount of chemical here is fixed due to the long-term aspects considered in the health hazard which mainly depend on the existence of hazardous chemicals for considering mitigation measures rather than on their amounts [89]. $I_j^H$ is an index of substance *j* for dangerous property in the health category.

$$E = \sum_{iE} \sum_j \left(z \, max_F \left(m_j^F\right) I_j^{iE}\right) + \sum_{iE} \sum_j \left(m_j^{out} I_j^{iE}\right) \tag{12}$$

where *z* is a fraction of the mass emitted to the environment in case of accident; $m_j^{out}$ is the specific amount of chemical substance *j* per kg of $CO_2$ captured under the same conditions as in LCA (e.g., 90% recovery and 98% mole purity) leaving the system to waste treatments units, for example, except for the product flow. $I_j^{iE}$ is an index of substance *j* for dangerous property *i* in the environmental category.

In addition to the single E, H, and S scores calculated for the capture systems, potential of danger (PoD) was also computed, which evaluates the magnitude of EHS effects by a physical unit, for instance, releasable energy content of the system or the volume of air/water required to dilute a dangerous chemical[67]. The overall impact is a combination of the potentials

of danger for all the chemicals used or formed during the capture process. The potential of danger was calculated by Eq. 13[67].

$$PoD_{ij} = m_i \times 10^{a_{i \times I_j} - b_i} \quad (13)$$

where $PoD_{ij}$ is a potential of danger for chemical *i* for *j* dangerous property, $I_j$ is a dangerous property index; $m_i$ is the maximum mass of substance in the process per kg $CO_2$ captured under the same conditions as in LCA (e.g., 90% recovery and 98% mole purity), and $a_i$ and $b_i$ are exponential parameters [90].

PoDs were determined in order to perform multicriteria assessment and evaluate outstanding impacts of single substances in specific categories. The PoD values allow comparison of different chemicals of the system at the level of dangerous properties to identify which chemical is potentially responsible for the most impact.

### 3.2.3 The most uncertain aspects of the assessment

There are many studies addressing such aspects of the phase-change solvent systems as reboiler duty, $CO_2$ absorption rate, mass transfer performance and phase separation, but little attention is given to aspects like solvent production processes, possible degradation behavior of the phase-change solvent alternative or emissions intensity. While all the aspects are expected to be similar to the performance of the conventional capture solvents, different process design and capture conditions of the phase-change systems can influence the magnitude of the effects, which should somehow be estimated to perform the holistic assessment.

*Thermal and oxidative degradation*

The degradation of the solvent might be the most uncertain aspect of the phase-change based capture process. To date, there are no or very limited data on degradation behaviour of the phase-change solvents. For that reason, estimation of degradation rate and nature of the products formed during the degradation was done on the basis of the available lab experimental data in relation to industrial data for MEA. In case there are no lab experiments conducted on the phase-change solvents, structurally similar compounds were used for approximations. The effect of the uncertainty was analysed by different degradation scenarios.

From the studies made on the conventional solvents, it is known that solvent molecules tend to degrade oxidatively and thermally during the capture process. The oxidative degradation is caused by $O_2$ coming in with the flue gas and mainly occurs in the absorber and the cross-exchanger. Thermal degradation mainly takes place in the stripper in the presence of $CO_2$ and high temperatures. Degradation is influenced by various factors including solvent composition, molecular structure, process operation conditions, characteristics of the flue gas etc. While both types of degradation happen in the $CO_2$ capture system, the oxidative degradation is expected to be responsible for the majority of phase-change solvent loss. Since lower temperatures are required to recover phase-change solvents, thermal degradation is believed to be low [16].

*Fugitive emissions*

Harmful molecules of the solvent and degradation products might be released to the environment when the treated flue gas leaves the absorber. It has been reported that emissions from the $CO_2$ capture plants can be increased up to two orders of magnitude because of the aerosols generated in the column. For this assessment, it was assumed that the aerosol formation would increase the emissions by one order of magnitude, but the majority of these increased emissions were avoided due to a $NO_x/SO_x$ wet scrubber and the wash columns with installed demisters treating the off gas leaving the absorber. The aerosol formation is a complex phenomenon affected by various factors like quality of the flue gas (especially presence of soot and $H_2SO_4$ [91] ), volatility of the solvent, operational conditions and packing of the columns[92], making it difficult to estimate and control[93].

*Auxiliary materials*

With the exception of the main solvent process, the process of the carbon capture by chemical absorption requires use of additional chemical auxiliaries to pretreat the flue gas, to reduce the degradation of the solvent, to prevent emissions of harmful substances to the environment and to reduce problems like foaming, corrosion, fouling and plugging in the equipment. Extra chemicals are also applied to treat the waste generated during the process operation.

The assumptions regarding the auxiliary materials were, to a large extent, based on the information for the conventional MEA-based capture systems and estimations models. However, such process complications like foaming, corrosion, fouling and plugging were omitted from the assessment due to the limited availability of data to predict and quantify them.

*Production of the solvent*

The impact of the solvent production influences the LCA impact of the whole capture system if the solvent experiences significant losses and requires constant replenishing during the capture process. LCA impact of the solvent production was estimated by the FineChem models and was defined by the complexity of the synthesized molecule. Longer chain molecules especially those containing quaternary centers[94,95] might be more difficult to synthesize leading to the increased consumption energy and material resources, thus, increasing the impact of the production. However, FineChem prediction is subjected to uncertainty. The model was trained on a dataset of 392 cradle-to-gate inventory data of organic chemicals. Its prediction capacity (assessed by the coefficient of determination) varies from 0.41 to 0.58, the lowest being for GWP and the highest being for the CED prediction.

The EHS assessment of the solvent production process was currently excluded due to high uncertainty associated with the process of the solvent production.

### 3.2.4 Exposure analysis

Exposure analysis evaluated process specific hazards like leakages or spills, which might lead to exposure of workers to harmful substances present in the capture system. Occupational exposure concentrations (OELs) representing maximum airborne concentration of chemicals to

which workers can be exposed over a period of time without experiencing adverse health effects[96] have been established for many chemicals. Concentration of chemicals leading to the adverse health effects following dermal or oral exposure to a substance is given as an acute toxicity limit expressed as LD50 (oral, dermal) or LC50 (inhalation)[97]. OELs and acute toxicity chemicals are provided by manufacturers in material safety data sheets (MSDS) of chemicals or can be found in databases[98,99] or chemical directories and guidelines. In case there are no experimental data, estimation methods like, GC for PEL (permissible exposure level) could be used.

Exposure of workers to chemicals at the capture plant is likely to happen mostly via inhalation, when chemicals are emitted directly from the equipment or volatilize from accidental spills. Fugitive emissions, leakages and spills are seen as more dangerous ways of exposure, than cleaning or maintaining of equipment since workers are not wearing protective apparel and not taking precautions [68]. In the assessment, fugitive emissions of chemicals at the top of the absorber were assumed to be reduced to the concentrations below OELs due to implementation of demisters, washing sections, and pre-treatment of the flue gas. Thus, exposure analysis in this study was applied to estimate if leakages or spills of the solvents might pose a hazard to personnel of the capture plant. Special attention was given to the accumulation of carcinogenic nitrosamines in the system above safe levels that might result in dangerous concentrations in the working environment in case of the leakage or spill.

The main focus of the analysis was exposure to solvent via leakages (long-term) and spills (short-term) and accumulation in the system of nitrosamines above safety levels of 13.7-14 mM[68,100] leading to harmful concentrations of the nitrosamines in the air. The estimation of the solvent concentration in air in case of leakage or spill was estimated by the equations provided by Nicas (2016)[101] and Keil and Nicas (2003)[102]. A leakage case assumed a constant amount of the solvent being released to the working environment at constant evaporation rate. Very small, difficult to detect, amounts of the solvent leakage were assumed, causing longer periods of exposure. Thus, the resulting air concentration of the solvent was compared to regulatory TWA (time-weighted average) limit for 8-hour workday repeated exposure with no adverse effects. In case of a spill, different volume spills were assessed at decreasing-with-time emission rate. Dangerous-to-health air concentrations for the solvent were assumed to occur during the first seconds of the spill. The air concentration values were compared to IDHLs (immediately dangerous to life or health) or inhalation toxicity LC50 limits for humans, indicating possible adverse effects induced by the exposure. In both cases the air concentration of the solvent was also calculated after 15 min of the leakage or spill accident, and was compared to STEL (short-term exposure) or TWA to evaluate if safe concentrations were reached within that period of 15 min.

Unlike the solvent, the concentration profile of nitrosamines in the system is unknown, thus a different approach was required to assess the exposure to nitrosamines. To avoid dangerous concentration of nitrosamines in the air, potential steady state concentration of nitrosamines[100] in the system was calculated and compared to the safe levels.

More details on the methodology are given in Paper III and in Supplementary material to Paper III.

# 4 Main findings

## 4.1 Substance level

Pareto fronts for some property categories obtained during the simultaneous CAMD with the integrated sustainability assessment of the molecules are visualized in Figure 4-1 as Case 2. Case 1 depicts the results of the CAMD without the use of the sustainability indices but instead performing the sustainability assessment of the molecules obtained by CAMD as a post-design step. The highest performing structures are presented in Table 4-1. It can be noticed that use of the sustainability criteria led to the identification of a wider set of structures in the obtained Pareto front (~100 structures), compared to having only thermodynamic properties as objective functions in CAMD (Case 1, ~40 structures). The search, however, was found to be biased towards OH-containing molecules, which are preferable from the sustainability point of view but might be less beneficial in terms of phase-change due to higher polarity and hence, miscibility in water as a result of the strong hydrogen bonds of OH-group and water (See Figure 4-2). Nevertheless, OH-containing molecules were identified as possible solutions, satisfying the constraint of the Hansen solubility parameter difference to water, indicating the phase-change behaviour. Thus, molecules with -OH group may still exhibit the phase-change behaviour but to, perhaps, less extent. This remains to be tested with advanced group-contribution methods and/or experiments.

The increased polarity and ability to form strong hydrogen bonds reduces the mobility and boiling and flash points of the OH-containing molecules, decreasing hazards associated with health and safety. Furthermore, the increased hydrophilicity due to their polarity makes OH-group containing molecules less toxic to aquatic life. Such an effect could be explained by hydrophilic groups being less likely to attach to lipids of living cells[103]. The beneficial performance of the OH-containing molecules (alkanolamines) in terms of GWP and EI99 index has also been observed. This might be associated by the substitution of an alkyl for a OH- group that lowers the number of the potential isomers containing quaternary carbon or nitrogen bearing centres (atoms with four substitutes). The quaternary centres are characterised by elevated impact values due to difficulty to synthesize them[94,95]. By contrast, the CED values of the alkanolamines (estimated by the FineChem) were observed to be slightly higher than those predicted for the alkanamines. That might indicate more energy-intensive alkanolamine production process compared to alkyl-containing compounds or be the result of uncertainty introduced by the FineChem prediction.

Phase-change characteristics determining energy and cost penalty of the $CO_2$ capture are the main drivers of the adoption of the technology; thus, this solvent feature might need to be prioritized. In that case, the decomposed approach where strong phase-change candidates are identified with the means of CAMD as a first step and then further screening is performed according to their sustainability assessment as a second step may be preferred. However, the simultaneous approach resulting in the wider set of structures in the Pareto fronts, still contained similar structures to ones proposed by the decomposed approach but also proposed new OH-containing molecules exhibiting phase-change behaviour. This kind of molecules have not been

investigated to the same extent as alkane- or other types of non-OH amines and require more attention. The detailed analysis of the results obtained for the both cases can be found in Paper II.

Additionally, the process of the integration of the sustainability framework to CAMD revealed the lack of reliable *in silico* methods to estimate properties of the molecules with missing experimental data. That motivated the idea of developing the hybrid prediction models. Even the first step of the hybrid model's development, namely the knowledge extraction, threw light upon the trends described above.

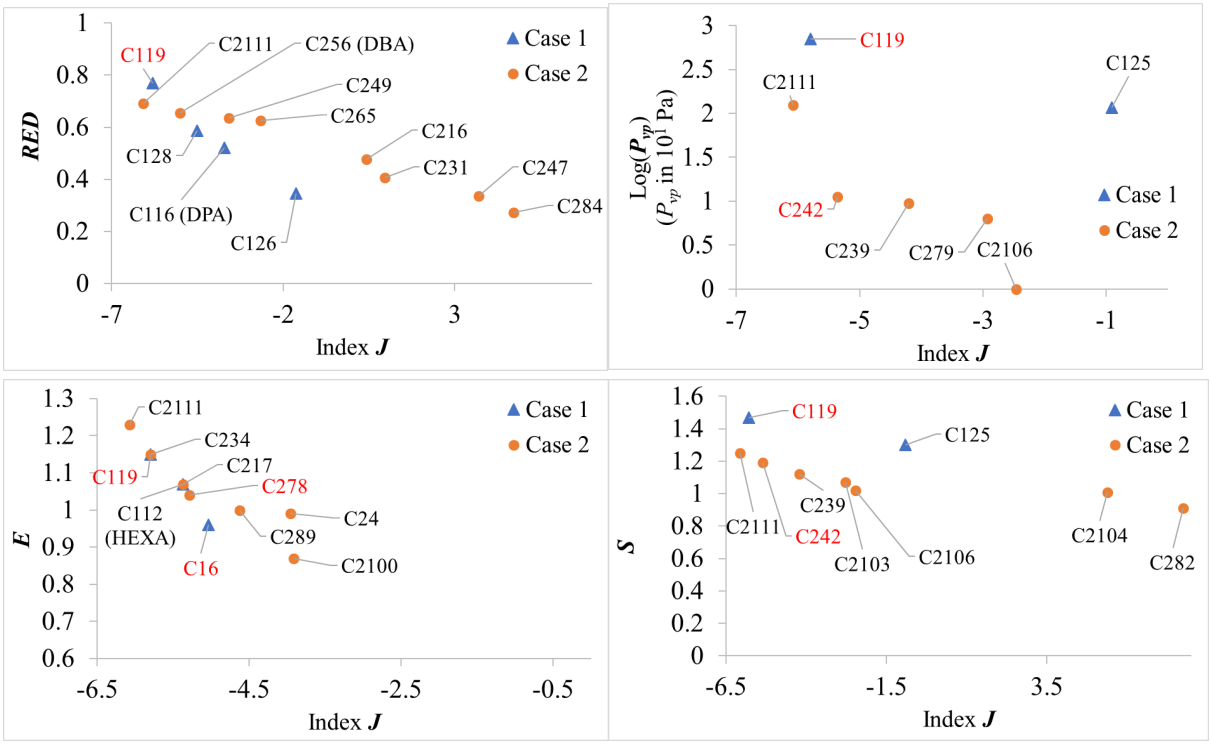



**Figure 4-1 Pareto points of the selected properties as function of index J for the molecular structures obtained after CAMD in Case 1 (triangles) and Case 2 (circles). ID numbers of molecules highlighted in red indicate high-performing options. Source: Paper II**

**Table 4-1 Highest-performing options among all structures designed in Cases 1 and 2, with *J* lower than -5. Adapted from Paper II**

| ID | Groups | Group frequency | ***GWP*** [kg $CO_2$-eq/kg] | ***CED*** [MJ-eq/kg] | ***EI99*** [Pt] | ***S*** | ***H*** | ***E*** |
|---|---|---|---|---|---|---|---|---|
| C2111 | [$CH_3$,$CH_2$,$CH_2NH_2$] | [1,6,1] | 3.58 | 93.45 | 0.3 | 1.25 | 0.18 | 1.23 |
| C234/ C119 | [$CH_3$,$CH_2$,$CH_2NH_2$] | [1,5,1] | 3.53 | 93.91 | 0.29 | 1.47 | 0.26 | 1.15 |
| C224/ C123 (DEEA) | [$CH_3$,$CH_2$,OH,$CH_2N$] | [2,3,1,1] | 3.31 | 107.38 | 0.23 | 1.49 | 0.19 | 1.24 |
| C217/ C112 (HEXA) | [$CH_3$,$CH_2$,$CH_2NH_2$] | [1,4,1] | 3.48 | 94.22 | 0.28 | 1.72 | 0.35 | 1.07 |
| C242 | [$CH_3$,$CH_2$,OH,CHNH] | [2,4,1,1] | 3.24 | 108.11 | 0.24 | 1.19 | 0.26 | 1.27 |
| C278 | [$CH_3$,$CH_2$,CH,OH,$CH_2N$] | [3,3,1,1,1] | 3.62 | 117.11 | 0.32 | 1.19 | 0.08 | 1.04 |
| C227 | [$CH_3$,$CH_2$,OH,CHNH] | [2,3,1,1] | 3.31 | 107.38 | 0.23 | 1.32 | 0.34 | 1.23 |
| C16 | [$CH_3$,CH,OH,$CH_2N$] | [3,1,1,1] | 3.38 | 106.67 | 0.23 | 1.86 | 0.34 | 0.96 |
| C256 (DBA) | [$CH_3$,$CH_2$,$CH_2NH$] | [2,5,1] | 3.58 | 93.45 | 0.3 | 1.54 | 0.18 | 1.07 |
| C116 (DPA) | [$CH_3$,$CH_2$,$CH_2NH$] | [2,3,1] | 3.48 | 94.22 | 0.28 | 2.07 | 0.38 | 1.05 |

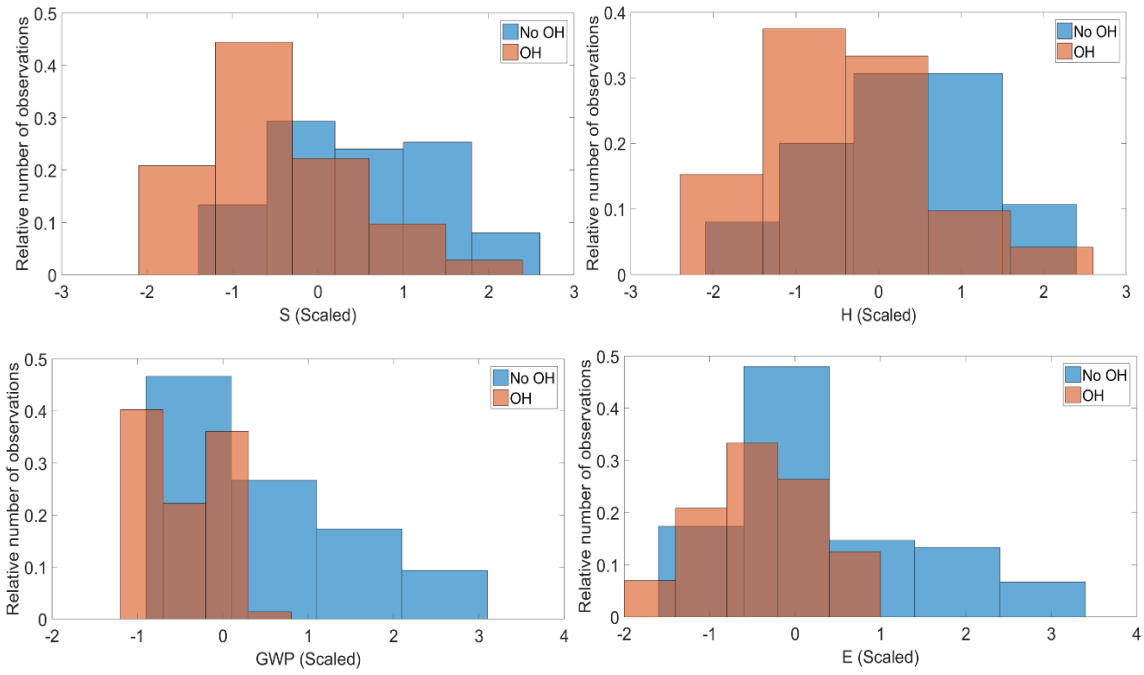



**Figure 4-2 Histograms showing molecular distributions for OH and no OH molecules in the selected property categories. The relative number of observations is the number of observations in the bin, divided by the total number of observations. Source: Paper II**

The process of the simultaneous CAMD with the sustainability assessment was then extended to include additional functional groups to design cyclic, and bi-functional (with 2 amino groups) amine structures. This led to identification of 120 solvent structures which were expanded into 624 isomers[104]. Among the designed structures experimentally verified phase-change solvents like DMCA (N,N-dimethylcyclohexanamine), MCA (N-methyl-cyclohexanamine), DPA (di-n-propylamine), HEPTA (heptanamine), and SBPA (N-sec-Butyl-n-propylamine)[16] were found. That pointed to the efficiency of the proposed approach in designing phase-change solvents that exhibit desirable $CO_2$ capture performance. The cyclic molecular structures have been also identified. The cyclic, multi-functional amines reported to have higher absorption capacity than mono-functional options, while exhibiting higher boiling point hence reducing the mobility and vapour losses of the solvent[16,105]. The analysis of the cyclic structures resulted in the selection of a novel solvent alternative – S1N (cyclohexylpropane-1,3-diamine) – due to its structural resemblance with the identified cyclic candidates but considerably lower price. Combined with DMCA, the solvent mixture exhibited high cyclic capacity and low regeneration energy requirements like other good phase-change solvents. More details on the whole solvent selection procedure and experimental testing results can be found in the work of Papadopoulos et al., 2020[104].

## 4.2 Process level

The environmental, health, and safety assessment at the process level evaluated the performance of the phase-change solvent-based systems mitigating the emissions from two reference plants: a quick lime plant, producing 150 tonne of lime per day, and a 400 MW natural gas combined cycle power plant. The compositions of the flue gases differ in the content of $CO_2$, $O_2$, $NO_x$ and $SO_x$. Flue gas of the lime plant contains 3 times (mol %) more $CO_2$ and significant amounts of $SO_x$ and $NO_x$ (350 and 400 mg/Nm$^3$), compared to the flue gas coming from the power plant carrying much lower $NO_x$ (21 mg/Nm$^3$) and no $SO_x$ but twice as much $O_2$. Both gases contain soot.

The $CO_2$ capture processes with two selected solvents for the two reference plants were designed with the usage of a shortcut model of an absorption/desorption system for $CO_2$ capture. The model provided an assessment of the reboiler duty required in the desorber[106]. The shortcut model accounted for the non-ideal behaviour of the solvents by considering the vapour-liquid-liquid phase-equilibrium (VLLE) relation for each solvent. The model used this relation, obtained from the experimental data during the pilot plot testing, in order to calculate the energetic requirements of the desorption based on various process operating parameters, such as the mass flowrate, the solvent lean and rich loadings, temperatures and pressure. The processes were optimized for the solvents based on the minimization of the total cost the process[106].

Two phase-change solvent alternatives were studied: a novel mixture of S1N and DMCA identified by means of CAMD[104] and the known phase change solvent MCA[16]. In the solvent mixture, S1N, containing both primary and secondary amine groups, serves as an absorption activator, while DMCA acts as a regeneration promoter[104]. During the phase-separation

hydrophilic S1N tends to accumulate in the water phase, while hydrophobic DMCA is concentrated in the organic phase.

In the S1N+DMCA-based capture system, $CO_2$-rich flow contains significant amounts of water, whereas the $CO_2$ -lean phase, recycled back to the absorber, carries half the amount of $CO_2$ and a small amount of water[107]. By comparison, the $CO_2$-lean flow of the MCA system consists of water and a very small amount of $CO_2$. The S1N+DMCA and MCA solvents capture systems differ also in the placement of the liquid-liquid phase-separator. In the process that uses S1N+DMCA, the phase-separator is placed before the intermediate heat exchanger because the liquid-liquid phase-split appears at 40ºC. In the process using MCA, the phase-separator is placed after the intermediate heat exchanger because the phase-split appears at 90ºC.

Both S1N+DMCA and MCA solvents showed a beneficial performance in terms of rich loading and cyclic capacity compared to the performance of MEA. The main operating parameters of the capture systems are presented in Table 4-2. More details on the generation of the process flowsheets can be found in the work of Kazepidis et al. (2020)[106] and Paper III.

**Table 4-2 Critical operating parameters of the optimized systems[107]. Source: Paper III**

| | S1N+DMCA Lime plant | S1N+DMCA Power plant** | MCA Lime plant | MCA Power plant |
|---|---|---|---|---|
| Solvent per $CO_2$ captured, kg/tonne $CO_2$ | 11000 | 10000 | 8000 | 14000 |
| $\frac{G_{mol}}{L}$, mol/l* | 6.7 | 23.5 | 7.93 | 16.1 |
| Temperature in the absorber, °C | 45 | 45 | 73 | 71 |
| Solvent regeneration temperature, °C | 90 | 85 | 106 | 101 |
| Reboiler duty, MJ/tonne $CO_2$ | 2340 | 2083 | 2346 | 2091 |

*Inlet flue gas flow to circulating liquid flow rate

**The lower solvent flow for the same plant case is an effect of economic optimisation of the flowsheets, which decrease the solvent flow in relation to its price, rather than solvent properties. S1N is considerably more expensive than MCA

To perform the environmental, health, and safety assessment of the designed capture units, the material flows derived via optimization procedure[107] had been adjusted to incorporate aspects which are important for the LCA and EHS hazard assessment of the system that were not tested experimentally, such as loss of the solvent due to degradation, aerosol formation and solvent reclaiming. Additionally, material flows of the auxiliary units (e.g. pre-treatment of the flue gas for the power plant case, washing of the treated flue gas and wastewater treatment) were added.

*Degradation of the solvents*

Degradation of the solvent molecules is one of the main causes of the solvent loss during the capturing process. Estimation of the solvent loss early during the design of the process relies on the availability of experimental studies, which are limited for novel materials like phase-change solvents. In the case of MCA and DMCA, there are experimental tests performed by Zhang (2013)[16] assessing the oxidative and thermal degradation of the molecules. According to the results, MCA might degrade 1.2-3 times more oxidatively and 2 times more thermally than MEA. DMCA, a tertiary sterically hindered amine, is reported to be stable to both oxidative and thermal degradation, degrading at lower rates than MEA. No experimental data on degradation behaviour exists for S1N. The degradation behaviour of the structurally similar molecules MAPA and MCA was used for the analysis. According to this, the lowest oxidative degradation ratio was assumed to be between 3 and 10 times of the degradation rate of the MEA.

Allylamine and propyl formamide were taken as the main degradation compounds of S1N. Ammonia and other amines were assumed for DMCA. Ammonia and cyclohexanone oxime were believed to be formed in the MCA system. Based on the assumptions regarding the degradation behaviour of the solvent molecules, different scenarios were assessed.

*Auxiliary units*

The purge of the lean solvent stream going to the reclaimer was taken in the amount keeping the steady-state concentration of the non-volatile degradation products below 1.5 wt. % in the circulating flow. The reclaimer waste flows were estimated assuming 5% loss of the purged flow in the reclaimer[108]. To remove the volatile degradation products in the flow of the treated flue gas leaving the absorber, washing sections were modelled with the help of Aspen Plus ®. Acid and water wash were assumed for the MCA system, where ammonia is expected to be generated. Only the water wash was modelled for the S1N+DMCA system to capture allylamine, which is volatile and highly soluble in water. The flows of the washing section were estimated on the basis of the assumption that the aerosol formation would increase the volatile emissions by one order of magnitude, but the majority of these emissions were avoided due to a $NO_x/SO_x$ wet scrubber. The $NO_x/SO_x$ scrubber was assumed only for the power plant flue gas containing elevated levels of $SO_x$ and $NO_x$.

The detailed analysis of the possible degradation behaviour of the solvent molecules, degradation scenarios considered, and all the introduced assumptions can be found in Paper III.

### 4.2.1 LCA

The results of the LCA performed on the carbon capture phase-change systems with the selected solvents are presented in Figure 4-3. The net $CO_2$ savings range from 0.33 to 0.47 kg-$CO_2$ per kg-$CO_2$ captured for the various investigated cases. It can be seen that the main contributor to the overall environmental impact for all the systems in all three life cycle impact categories is steam for solvent regeneration, followed by electricity required to deliver sea water

for the cooling processes. However, the impacts of the remaining contributors vary depending on the system and the impact category. The flue gas of the power plant is characterised by a lower level of $CO_2$ (3.6 vol%), compared to the flue gas of the lime plant (12.3 vol%). This explains the almost three times higher impact coming from the flue gas blower and increased amount of cooling media to reduce the temperature of the flue gas to required temperature for the absorption (40ºC).

The lowest overall impact is observed for the MCA lime plant-based capture system which has the smallest loss of the solvent due to the degradation and the smallest amount of the solvent flow required to capture 1 tonne of $CO_2$. The MCA lime plant system also shows the best performance if the highest solvent degradation rates are applied (See Figure 4-3, dashed lines). By contrast, S1N+DMCA the system demonstrates the most severe performance changes, depending on the highest or lowest solvent degradation rates being applied for the assessment. For the case with the minimum degradation rate, the highest impact is observed for the MCA Power plant, containing the largest flow of the solvent per tonne $CO_2$, while the environmental performance of the other three systems is similar. The high solvent degradation rate has a considerable effect on the impact of the S1N+DMCA system, where the worst possible degradation rate was assumed to be 10 times higher than the degradation rate of the conventional solvent MEA. In that case, the impact increase is explained by the elevated degradation loss of the solvent resulting in the higher flow of the solvent make-up, additional burden on the reclaimer dealing with the products of the degradation and impact coming from the reclaimer waste treatment.

It can be concluded that use of renewable electricity and industrial waste heat (i.e., at 90-100ºC) can decrease the LCA impact of the phase-change capture unit by 70-90%. Then, the remaining impact will be dominated by the degradation behaviour of the solvent molecules. The detailed analysis of the LCA results for various solvent degradation scenarios can be found in Paper III.

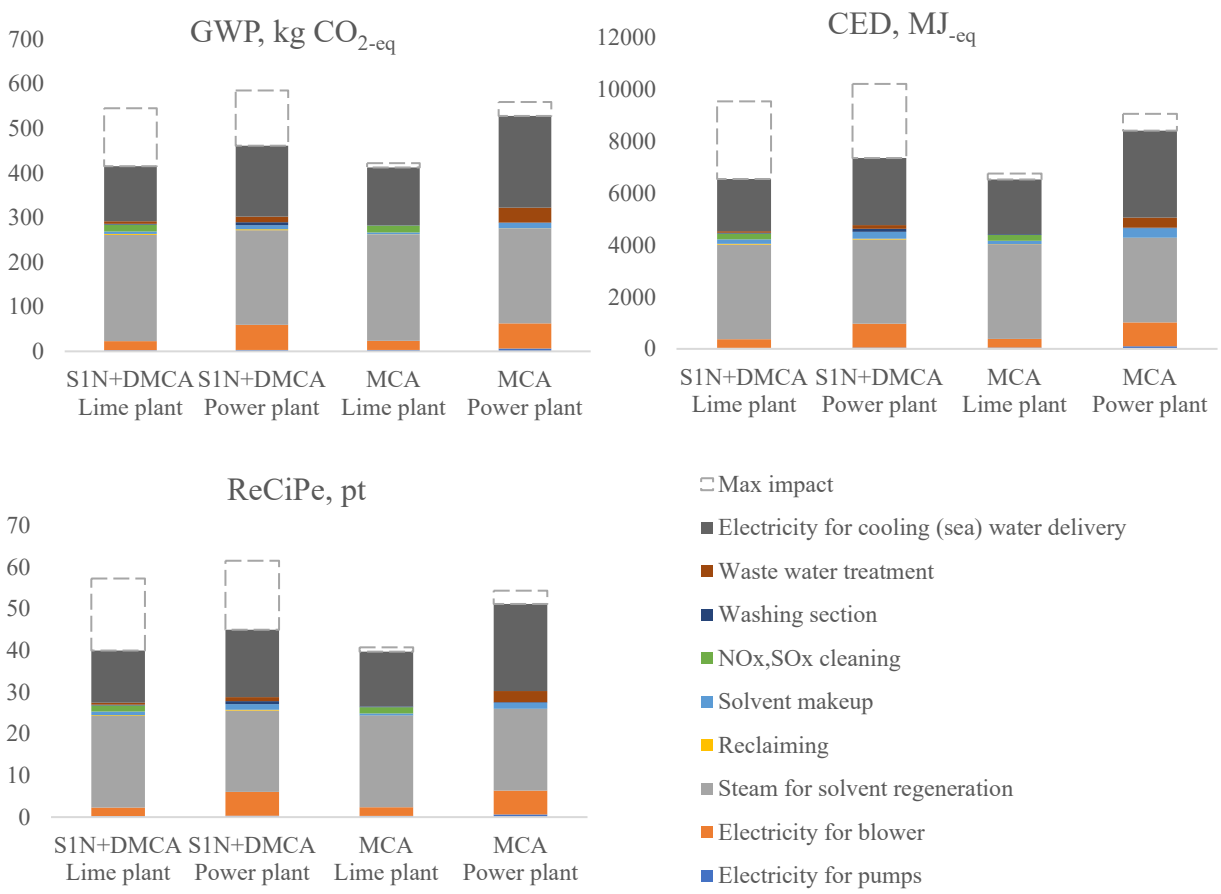



**Figure 4-3 Contributors to the LCA impact per tonne $CO_2$ captured based on the scenarios with the minimum degradation rate of the solvent. Dashed lines indicate the increase in the impact if the highest degradation rate of the solvent is applied. Adapted from Paper III**

### 4.2.2 EHS

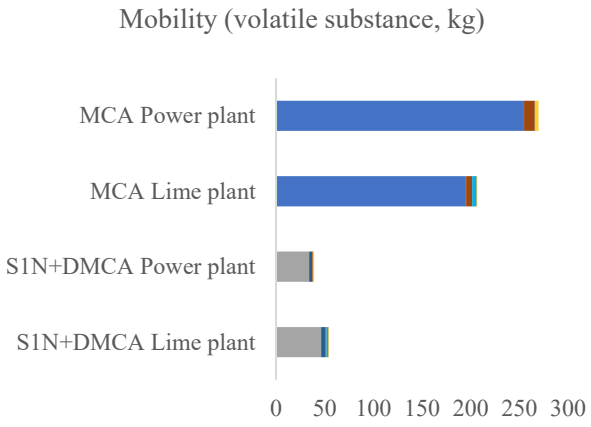
The solvent molecules, the auxiliary process chemicals as well as various compounds formed during the degradation of the solvent molecules can be hazardous for working personnel and the environment. EHS hazard impact of the chemical is defined by inherent properties of the chemical to cause harm to human health and the environment and mass of the chemical in the process, which scales the inherent hazardous potential of the chemical. The contribution of every chemical present in the system to the potentials of danger in some of the EHS subcategories is shown in Figure 4-4. It can be seen that in the mobility and water mediated effects the overall impact is dominated by the mass of the solvent molecules, present in the system in the greatest amount compared to all the other chemicals. In comparison, the potential of danger in chronic toxicity and air mediated effects is defined by the inherent property of the chemicals, namely occupational exposure limits (See subchapter 3.2), indicating toxicity of some substances to human health even in small concentrations.

High mobility of the MCA due to its lower boiling point compared to DMCA and S1N defines its highest impact in the Safety category. It is followed by the impact of the DMCA molecule with the similar boiling point dominating the overall impact of the S1N+DMCA carbon capture system. However, the impact of the S1N+DMCA is considerably lower due to the less amount of mobile DMCA solvent used for capture of 1 tonne of $CO_2$ in comparison to MCA. Among the three solvent molecules, the S1N molecule has the highest boiling point, thus exhibits lowest hazard in terms of plant safety.

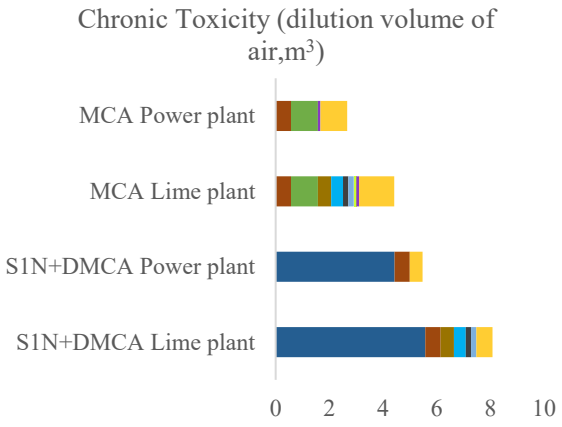
The large mass flow of the phase-change solvents circulating in the capture system increases the risk of the solvents being emitted to water sources, affecting aquatic life. Considerable contributions to water mediated effects are observed for sodium hypochlorite (NaOCL) and sodium nitrite ($NaNO_2$), substances present in the pretreatment of the lime plant flue gas. These chemicals are highly toxic to aquatic life.

High chronic toxicity to human health is expected from the allylamine, ammonia, nitrosamines formed during the degradation of the solvent molecules and also auxiliary chemicals like sulfuric acid ($H_2SO_4$), NaOCL, sodium hydroxide (NaOH) if people are frequently exposed to these substances. The health category is independent of mass, and so the impacts are based on the inherent toxicity property of these chemicals.

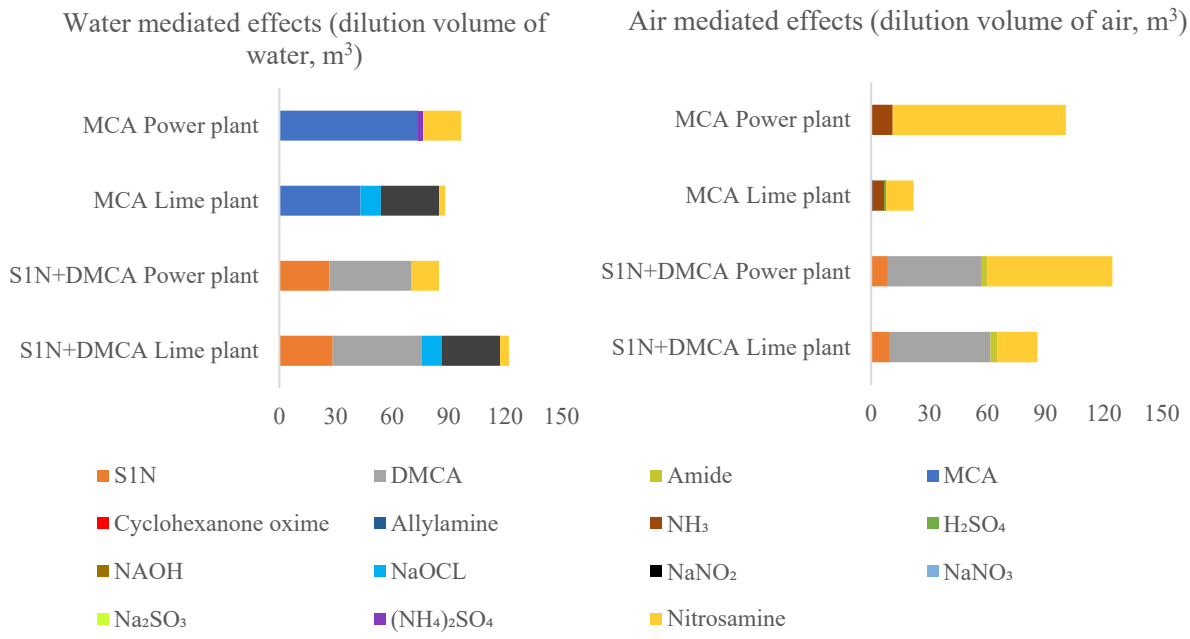
The air mediated effects rely on the mass and toxicity property of the chemicals, hence significant contribution of the DMCA and S1N solvent molecules is observed. MCA does not appear in the air mediated effects because of its much lower chronic toxicity (PEL = 235 mg/m$^3$) to humans compared to DMCA (PEL = 5 mg/m$^3$) and S1N (PEL = 10 mg/m$^3$). Significant impact is expected to come from nitrosamines because of their harmful effect to humans even at very small concentrations (2.39 mg/m$^3$ [68]). The highest levels of steady state concentrations of nitrosamines are expected for the power plant-based capture systems as result of their lower stripper temperatures and increased inlet flue gas flow to circulating liquid flow. The graphs for all the subcategories with the detailed analysis can be found in Paper III. The accumulation of the nitrosamines was also separately studied in the exposure analysis part.




a. Safety




b. Health




c. Environment

**Figure 4-4 Examples of the Potential of danger per tonne of $CO_2$ captured in different categories (Health category uses fixed mass of 1 kg) at $NO_x$= 5 ppm. $CO_2$, $H_2O$, $O_2$ and $N_2$ molecules are considered as non-hazardous and omitted. Note: average values between different scenarios are presented, and only chemicals with contribution more than 2% are shown. Source: Paper III**

The multicriteria assessment for the MCA and S1N+DMCA $CO_2$ capture systems is presented in Figure 4-5. The impact of the studied carbon capture systems is normalized to the impact of the conventional MEA based system[68,109] (See Table 4-3). The phase-change systems show beneficial performance in terms of the reboiler duty, the H, E, CED, and GWP values compared to the MEA. However, it should be noted that the results are a first indication; more experimental data, especially on solvent degradation is required to have more accurate comparison.

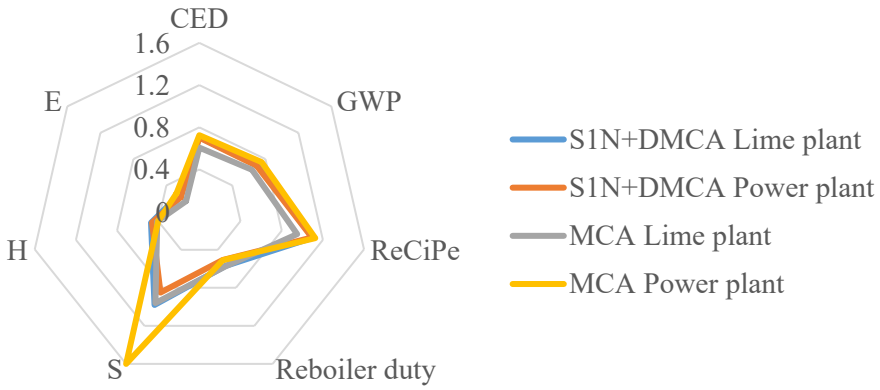



**Figure 4-5 Multicriteria comparison of environmental, health and safety impact of the different solvent systems for $CO_2$ capture normalized to the impact of the conventional MEA system.**

**Table 4-3 MEA system impact data taken for the multicriteria comparison. All the values are given per tonne of $CO_2$ captured**

| | Reboiler duty, GJ | S | H | E | CED, $MJ_{-eq}$ | GWP, kg $CO_{2-eq}$ | ReCiPe**, pt |
|---|---|---|---|---|---|---|---|
| MEA* | 4.1 | 15369.6 | 2.0 | 4433.2 | 10000.0 | 600.0 | 38.6 |

*A conventional MEA (30wt%) based carbon capture system at solvent regeneration temperature 120°C. The solvent rich and lean loading is 0.49 and 0.2 mol $CO_2$/mol solvent, respectively[109].
**The ReCiPe is calculated from EI99 value on the basis of the correlation[88].

### 4.2.3 Exposure analysis

In case there are leakages or spills of the solvent in the capture plant, the solvent concentration in the breathing air might pose a danger to the health of the workers. The exposure analysis aims to evaluate if leakage and spills accidents could pose a hazard to personnel working in near proximity and farther away from the place of the accident. The analysis showed that for the MCA capture system, leakages and spills of the solvent up to 1000 ml do not pose a hazard to humans, however, special care should be taken for spills of larger volumes, especially of pure MCA (See Figure 4-6a). For the S1N+DMCA solvent system, the analysis demonstrated that leakages of pure solvents or solvent mixture do not result in air concentrations of concern for DMCA or for S1N. However, spills of pure DMCA and solvent mixture leaving the stripper might pose immediate danger to health of the workers (i.e., due to the resulting air concentrations of DMCA) when the spill volume is bigger than 100 ml (See Figure 4-6b,c).

The estimation of the steady-state concentrations of nitrosamines in the circulating flow of the solvent showed that nitrosamines could reach and go beyond safety threshold values (13.7-14 mM[68,100]), leading to dangerous concentration of the nitrosamines in the working environment. For the power plant-based $CO_2$ capture case, this can happen already at $NO_x$ equal to 5 ppm for the S1N + DMCA and 10 ppm for the MCA solvent systems. The lower $NO_x$ limits for the power plant based S1N+DMCA systems can be explained by the higher gas-to-liquid ratio and slightly lower stripper temperatures. The detailed analysis can be found in Paper III.

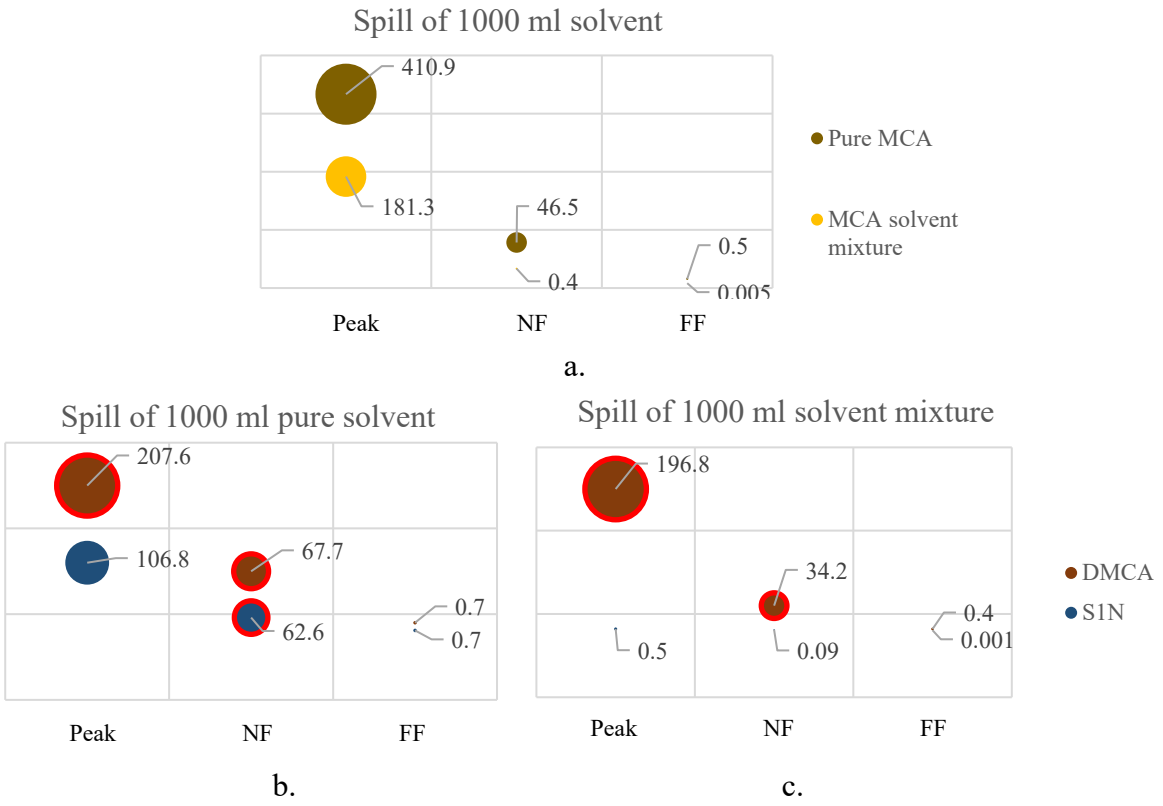



**Figure 4-6 Air concentration of MCA (a) , DMCA and S1N (b,c) (mg/m$^3$) in case of 1000 ml spill of the solvent. Peak is the concentration during the first seconds of the spill, NF- concentration in the near field (1 m from the center of the spill), FF - concentration in the far field (10 m from the center of the spill). Bubles marked with red outline indicate values exceeding the safe limits. Source: Paper III**

# 5 Conclusions

The work addressed the environmental, health, and safety aspects of post combustion capture systems deploying phase-change solvents. The evaluation was done at both substance, and process levels. At the substance level assessment, the LCA and EHS hazard assessment impact associated with the solvent molecules was used as additional criteria during the solvent design and selection procedure, whereas the process level assessment focused on the probable impact of the capture system when certain phase-change solvents are used in the capture process. Additionally, automated computation of the molecular properties necessary for the assessment was established.

The results of the incorporation of the impact indices into the solvent design procedure showed that a much wider set of optimal solvent structures was identified compared to having only thermodynamic properties as objective functions in CAMD. However, the search was biased to the OH group containing molecular structures exhibiting lower impact, which show a higher solubility in water and thus might be not beneficial from the phase-change perspective. However, even though the majority of phase-change solvents for $CO_2$ capture previously investigated in published literature are alkane-amines, in few cases OH-containing amines have also been proven to exhibit liquid-liquid separation which have so far received considerably less attention and require further investigation. The use of the solvent with the most favourable safety and health impact performance might be a more attractive option for industrial large-scale application due to the reduced demand for safety and control measures.

Furthermore, the work revealed the lack of reliable *in silico* methods to estimate properties of the molecules with missing experimental data. In light of the EU legislation promoting the use of alternative *in vitro* or *in silico* approaches to replace the cruel animal testing there is a need for advanced models able to predict the properties of the molecules on the basis of available information.

The process level assessment showed that phase-change solvent systems have a potential to be a better alternative to the conventional amine solvent systems due to the reduced reboiler duty and first indications for the lower impact on the environment in terms of short-term and long-term EHS hazard related effects. The preference should be given to less mobile solvents which are clearly better with respect to plant safety. The main drawback could be that the process design of the capture systems with the phase-change solvents might promote accumulation of carcinogenic nitrosamines, thus their concentration should be carefully monitored. In terms of life cycle impact, the steam demand for solvent regeneration and the electricity required to deliver the cooling media were the main contributors to the impact. The use of renewable electricity and industrial waste heat (i.e., at 90-100$^{o}$C) can decrease the LCA impact of the phase-change capture plant by 70-90%. Then, the remaining impact will be dominated by the degradation behaviour of the solvent molecules, and therefore, experimental tests evaluating the degradation behaviour of the solvents as well as measures to reduce the degradation rates are of great importance.

# 6 Future work

Apart from the new solvent alternatives for $CO_2$ capture, new molecules are being constantly developed for novel applications in the (bio)chemical and power sectors (e.g., advanced functional materials, solvents for biorefinery, fluids for operation of organic Rankine cycles and heat pumps). In advanced computer-aided molecular design approaches, such molecules are first synthesized *in silico*, allowing for a vast number of molecular structures to be screened and assessed with respect to their technical and sustainability performance, before inferring a few optimal ones to proceed with experimental testing. Clearly, methods and tools are needed to rapidly predict the required properties of many different molecular structures for a large number of CAMD optimization iterations. Moreover, despite the constant exposure of humans and the environment to the existing chemicals, information on their impact on human health and environment is not always readily available[110].

Ideally, predictive models for sustainability related properties (e.g., hazard assessment) should be constructed based on molecular descriptors, first principles and/or semi-empirical models. These kinds of property predictive models (e.g., in the form of group contribution methods) have been reported for estimation of thermodynamic properties of molecules (e.g., vapor tensions, heat capacities, densities) and there are recent efforts to extend this approach to hazard assessment properties; however, only a few of the relevant properties are covered and not always with the same success in prediction accuracy as for thermodynamic properties.

It is possible to implement machine learning approaches to extract patterns from available data and predict properties of new molecules. However, selecting among a vast number of molecular descriptors and combinations thereof as predictor variables, while considering the limitations, uncertainties and even erroneous values in available property databases, makes the task of developing machine-learning based models with excellent generalization capabilities cumbersome. Thus, the aim of the future work is to develop a systematic method of extracting knowledge from a vast number of available sources in utilizable forms and combine it with machine-learning based models.

The work is to be performed in three main steps:

1) prior knowledge collection by text mining of research articles and reports published during the last 20 years.
2) development of a "pure" machine-learning prediction model (e.g., using different forms of machine-learning approaches) based on an available database of approx. 100,000 chemicals with relevant hazard assessment relevant properties
3) development of a "hybrid" machine-learning/prior knowledge model with improved generalization capabilities compared to existing group contribution models and the "pure" machine-learning based model of the previous step.

The first attempts to extract existing prior knowledge from the research articles has been performed and described in subchapter 3.1.3 and in Paper IV in more detail. Despite the successful extraction of some relevant knowledge, the method requires some adjustments and will be developed further.

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